Fundamental Study of Adhesion Problems

involving Polyethylene and other Polymers

by

Michael Boguslaw Konieczko

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ABSTRACT

The effect of existing pretreatments on polyethylene and to a lesser extent polypropylene, and the effect of two new pretreatments on polytetraflucroethylene were examined.

The pretreatments for polyethylene included chromic acid etching, corona discharge, flame treatment, nucleation in contact with aluminium and attack by organic liquids or their vapours. The behaviour of polyethylene as an adhesive for aluminium was also examined. The new pretreatments for polytetrafluoroethylene were, attack by electrochemically generated anions and direct contact with a polarised electrode.

Techniquies used to study the changes caused by the pretreatments included bond strength determinations, contact angle measurements, attenuated total reflectance spectroscopy, scanning electron microscopy and X-ray photoelectron spectroscopy.

The usefulness of X-ray photoelectron spectroscopy as a surface examining technique has been demonstrated by its ability to identify groups and give a measure of their concentration. As a result of its use it has been possible to show that polyethylene and polypropylene are oxidised on the surface by treatments previously considered not to cause oxidation. A relationship is shown to exist between oxidation and improved adhesion. Electrochemical treatments of polytetrafluoroethylene are shown to give rise to an oxidised surface layer, which leads to improved adhesion. Removal of this layer is shown to cause a considerable decrease in adhesion.

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This thesis is entirely my own work except where specifically stated. The work has not been submitted for another degree.

M.B. Konieczko

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I do not know what I may appear to the world, but to myself I seem to have been only like a boy playing on the sea-shore, and diverting myself in now and then finding a smoother pebble or a prettier shell than ordinary, whilst the great ocean of truth lay all undiscovered before me.

SIR ISAAC NEWTON
A short time before his death

1.1 General Introduction

Since the 1930's there has been an enormous increase in the use of thermoplastics. Many of the applications of these polymers require a satisfactory level of adhesion for the purposes of bonding, printing and coating. To achieve satisfactory adhesion it is usually necessary to pretreat these polymers. This programme involves the study of the adhesion problems of polyethylene and to a lesser extent polypropylene and polytetrafluoroethylene. In particular various surface treatments are examined in detail by a range of techniques.

1.2 Early development of polyethylene, polypropylene and polytetrafluoroethylene.

The history of polyethylene goes back to 1898, when von Pechman discovered that an ethereal solution of diazomethane produced a white substance on standing. In 1900 Bamberger and Tschirner analysed a similar product and showed that it had an empirical formula of $-(-CH_2-)_x-$.

In 1933 at ICI, R. O. Gibson and E.W. Fawcett while studying the effect of high pressures on various gases noted that with ethylene a white solid was formed. In 1935 8g of the polymer were prepared, and it was decided to proceed with development of the product. The first application should have been in the submarine cable industry. The first commercial plant was opened on September 1, 1939, and the whole production turned over to military use, in particular radar and ancillary equipment. The first polyethylene coated cable was not laid until 1945.

In 1950 Karl Zeigler found that in the presence of titanium chloride and alkyl aluminium, ethylene polmerised to form polyethylene with a

higher density than the ICI process. At about the same time the Phillips Company and the Standard Oil Company of Indiana developed processes for producing high density polyethylene, both employing supported transition metal oxides.

Guillio Natta following the work of Zeigler; discovered that Zeigler type catalysts could be used to produce isotactic polypropylene. The previously produced atactic polypropylene was of little commercial interest due to poor physical properties.

It was in the United States after the war that polyethylene production and processing became a large industry. Techniques for producing tubular lay flat film were invented, and the packaging industry turned to polyethylene. From the industry's point of view polyethylene had several advantages over its main rival, paper. It was not affected by water, did not tear easily, was clear in thin section and had a low water permeability. However, it was found that unlike paper it could not be printed. Also, there were no suitable adhesives and therefore it had to be heat sealed. This proved quite a serious limitation, since the sealing rate was limited to a few hundred bags per minute. Using adhesives with paper bags, the rate was in thousands per minute (1). Other processes such as printing, coating and metallizing required good adhesion. The lack of good adhesion proved a deterent to the wide acceptance of polyethylene, until methods of pretreating the surface were developed. Polytetrafluoroethylene (PTFE) was discovered by Plunkett, who cut open a cylinder of tetrafluoro-ethylene and found a white powder. PTFE is a tough, flexible, resilient material with excellent resistance to heat, chemicals and electric current. It has an extremely low coefficient of friction. However it has a high melting point and high melt viscosity, which

prevent the use of the normal techniques of thermoplastic processing. Like polyethylene it cannot be printed, coated, metallized or bonded without pretreatment.

1.3 Pretreatments

1.3.1 Pretreatments of polyethylene and polypropylene.

Many methods of pretreating polyethylene have been developed. The number of patents taken out is large and still increasing. The various pretreatments can be divided into three main groups, namely chemical, electrical and heat treatments. Historically, it is the chemical methods which take precedence. In 1946, the Visking Corporation (2) took out a patent for the surface chlorination of polyethylene. This involved passing chlorine gas over polyethylene, while subjecting it to UV radiation. Soon there were variations of this (3,4,5) and other gases such as ozone were also proposed (6). Other chemical treatments developed included treating with chromic acid (7), potassium permanganate in acid (8), acid perchlorate (9), aqueous persulphate (10) and more recently the USMC process (11). This involves coating the polyethylene surface with a sensitizer solution such as benzophenone in methylene chloride. The surface is then irradiated with UV light.

Heat treatment involves the polyethylene being subjected to intense heat for a short time as in flame treatment (12). Various sources of heat and different conditions have been proposed (13-14).

Electrical pretreatments are those where the films are passed through a high voltage discharge. Many variations have been used, among them corona discharge (15), glow discharge (16), and Tesla coil discharge (17). Bombardment with activated inert gases (CASING) has also been used (18). Other methods of treating surfaces have involved, melting against high

energy surfaces such as aluminium or gold (19), and more specifically for polypropylene, solvent etching (20) or using a primer (21). Commercially by far the most important methods are corona discharge for thin films and flame treatment for thicker sections such as bottles. Chromic acid is also used in special cases such as pretreatment of irregular objects, the insides of containers and also prior to metallizing polypropylene.

1.3.2 Pretreatments for PTFE.

The treatments for PTFE are more severe than those for polyethylene. The first treatment used involved immersing PTFE in a solution of an alkali metal such as sodium in anhydrous liquid ammonia. Alkali metal vapours such as lithium (22) have been used. Molten alloys (22) have been employed successfully. It has been found that alkali metal complexes with polycyclic aromatic hydrocarbons, such as sodium-naphthalene in tetrahydrofuran (23) react with the polymer surface to make it more receptive to bonding. CASING has been reported as being successful in treating the surface (18). More recently electrochemical methods of pretreating PTFE have been reported (24). These involve passing the polymer through a melt of sodium and potassium fluorides, while a current is passed.

1.4 Factors affecting adhesion

1.4.1 Surface structure.

When two dry, hard solids are pressed together, little effort is required to pull them apart. This occurs, because most solid surfaces are very irregular on the microscopic scale. So if two such surfaces are brought together there is very little real contact between them (fig.1). It is possible to use friction between the points of contact to cause

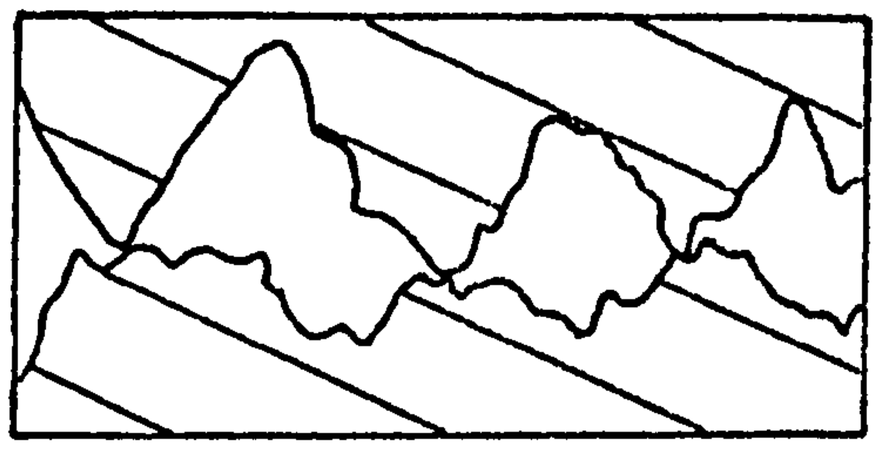


Fig.1
Contact between two solids

cold welding. However, Anderson (25) showed that this can only happen if the surfaces are free from contamination. He pressed two gold spheres together in vacuum. Good adhesion was only obtained when one of the spheres was twisted against the other. This caused the metal oxide and any other impurities to be sheared off, bringing areas of clean gold into intimate contact thus giving a good bond.

It has been known for a long while that strong adhesion can occur between carefully polished contacting solids if there is a liquid film between them. The liquid behaves as an adhesive by filling in the surface irregularities, increasing the area of contact and acts as a bridge (fig.2). Thus for an adhesive to perform its function well,

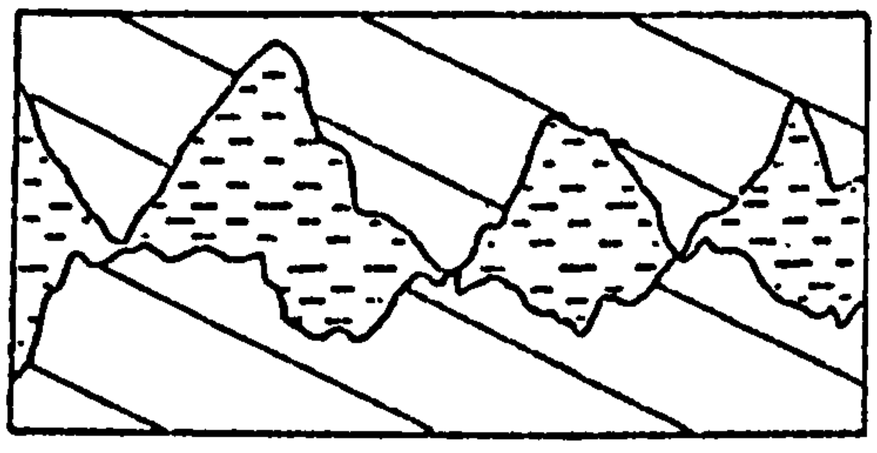


Fig.2
Two solids joined by an adhesive.

it must initially be sufficiently fluid to fill the surface irregularities. It must then solidify, with as little stress as possible and possess a high enough cohesive strength to withstand applied loads.

1.4.2 Surface Energy.

The degree of contact between an adhesive and a solid surface is dependent on two main factors. The first is the thermodynamic aspect and depends on the surface energies of the adhesive and the surface of the substrate. Basic to the subject of wetting is Young's (26) concept of contact angle Θ, between a drop of liquid and a plane solid surface. When Θ = 0, the liquid is said to wet the surface completely and will then spread freely over the surface, depending on its viscosity and roughness of the surface. When $\Theta > 0^{o}$ the liquid is non-spreading (fig.3). However, every liquid wets every solid to some extent and $\Theta \neq 180$. On a solid with a uniform surface, Θ is

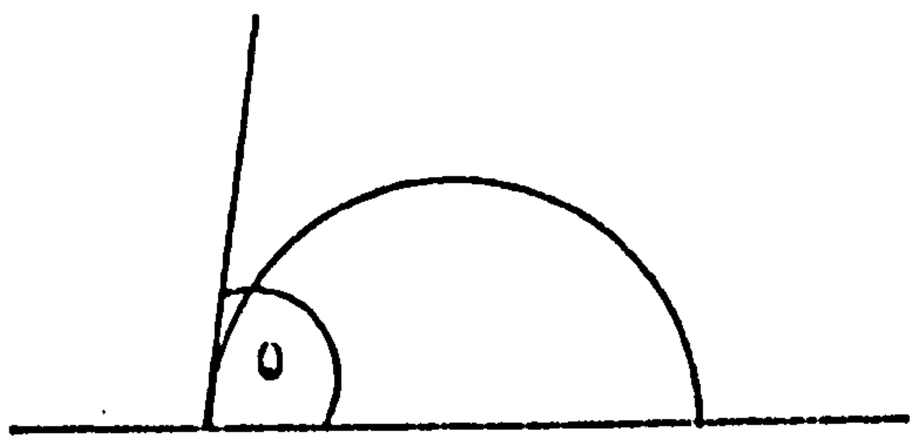


Fig.3
Contact angle of a drop

independent of the volume of the liquid drop. The tendency for the liquid to spread as Θ decreases, makes Θ a useful inverse measure of wettability.

Wenzel (27) showed that the contact angle as measured, Θ' depends on the roughness of the surface, r. This roughness factor, r, is related to the observed contact angle Θ', and the true contact angle, Θ by the relationship $r = \cos \Theta' / \cos \Theta$.

Young related the surface tensions γ_{sv^o}, γ_{sl} and γ_{lv^o}, existing at the phase boundaries of a liquid drop on a solid surface at equilibrium by the equation:-

$$\gamma_{sv^o} - \gamma_{sl} = \gamma_{lv^o} \cos \Theta$$

The subscripts sv^o and lv^o refer to the solid and liquid in equilibrium with the saturated vapour respectively. The contact angle Q, is measured at equilbrium. Dupre (28) related the reversible work of adhesion, Wa, of a liquid with a solid to the surface free energies by:-

$$Wa = \gamma_{s^o} + \gamma_{lv^o} - \gamma_{sl}$$

where s^o refers to the surface free energy of the solid in vacuum. Bangham and Razouk (29) recognising that the surface energy change due to adsorption of the vapour of the liquid on the surface of the solid cannot be neglected suggested that the reversible work of adhesion, Wa can be given by the equation:-

$$Wa = (\gamma_{s^o} - \gamma_{sv^o}) + \gamma_{lv^o} (1 + \cos Q)$$

Zisman and co workers (30) studied the equilibrium contact angles of a variety of pure liquids on solid surfaces. They found that there was a linear relationship between cos Q and the surface tension for each homologous series of organic liquids. By plotting cos Q against surface tension, and extrapolating the straight line to the horizontal line cos Q = 1, a value of surface tension, known as the critical surface surface tension of wetting, γ_c was obtained. Thus a liquid with a surface tension less than γ_c should spread on the surface. Real surfaces are neither flat nor free from pores. Thus their true surfaces areas are r times greater than the apparent. The work of adhesion will thus be r times greater than for the apparent area. However if the contact angle is large there will be difficulties in displacing air from the surface irregularities. For maximum adhesion and avoidance of stress concentration due to air bubbles the adhesive should penetrate and fill every crevice. An approximation for

capillary rise in a surface crevice is given by the equation (31):-

$$h = \frac{k\ \gamma_{lv}\upsilon \cos \theta}{R\ \varrho},$$

where h is the capillary rise, R, the radius of the capillary, $k = \frac{2}{981}$ and ϱ, is the density of the liquid. This equation only deals with the thermodynamic aspect of filling such a crevice. The Washburn-Rideal equation which deals with the kinetic aspect of filling a capillary is given as:-

$$t = \frac{2\eta\ h^2}{\gamma \cos \theta\ \ r},$$

where t, is the time required to travel a distance h in the capillary of radius r, and θ is the contact angle. This is important from the practical point of view since most adhesives are liquids only for a short time. The type of surface roughness will also affect the spread of the adhesive. Gentle curves are more likely to be filled easily than sharp crevices.

1.4.3 Viscosity.

As shown above the less viscous an adhesive is initially, the more likely it is to spread quickly and fill in at least some of the surface irregularities and achieve good contact. It has been pointed out by Wake (32), that increasing the degree of contact reduces stress concentrations due to voids and thus increases adhesion. Decreasing the viscosity of an adhesive, while solving one problem may lead to others. If the viscosity is reduced by increasing the temperature of application, stresses may arise on cooling, unless this is carried out slowly. Similarly, if viscosity is decreased by increasing solvent content, voids may occur during evaporation. While increasing the time the adhesive is in its low viscosity state is likely to lead to better contact and thus increase adhesion, in practice it may not be convenient for economic reasons.

1.4.4 Methods and conditions of testing.

It is perhaps rather paradoxical that adhesion is tested by measuring the force required to break a bond. The conditions during and after bond formation are important as are the conditions of test. During bond formation, conditions such as temperature, viscosity of adhesive, nature of the surface, and pressure will be important. Pressure will affect the degree of contact between adhesive and substrate, by forcing the adhesive into crevices. Increasing the temperature will affect the bond strength not only for the reasons mentioned above, but may also cause the loss of an essential component such as a low boiling hardener. This may lead to a decrease in bond strength Thickness of the adhesive is also important. Increasing the thickness of the adhesive layer decreases shear strength, probably due to an increase in stress concentrations.

The various test methods depend on four basic types of stress that can be used to test for adhesion. These stresses are tensile, shear, cleavage and peel.

In tensile loading the forces are perpendicular to the plane of the joint, and are thus uniformly distributed over the entire area of the joint. The whole system is under stress at the same time. No part of the joint carries a load different from the rest. When used for testing this type of joint is usually circular and is called a butt joint (fig.4).

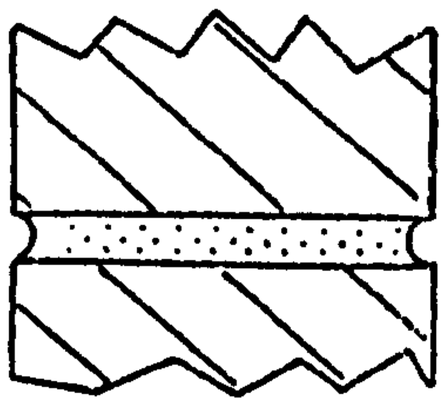


Fig.4
Butt joint

In shear loading the stress is parallel to the plane of the joint. As in the case of a butt joint the stress is distributed over the whole area uniformly. The simplest type of joint is known as a lap shear joint, and is frequently used in testing, because of ease of construction (fig.5). This type of joint is however prone to more

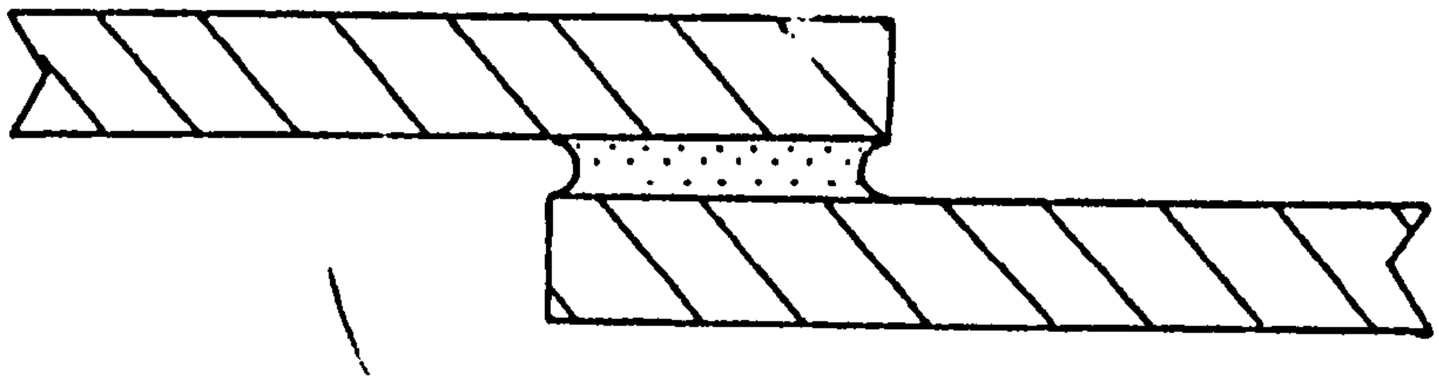


Fig.5
Lap shear joint

than one type of stress (fig.6). Distortion under load leads to

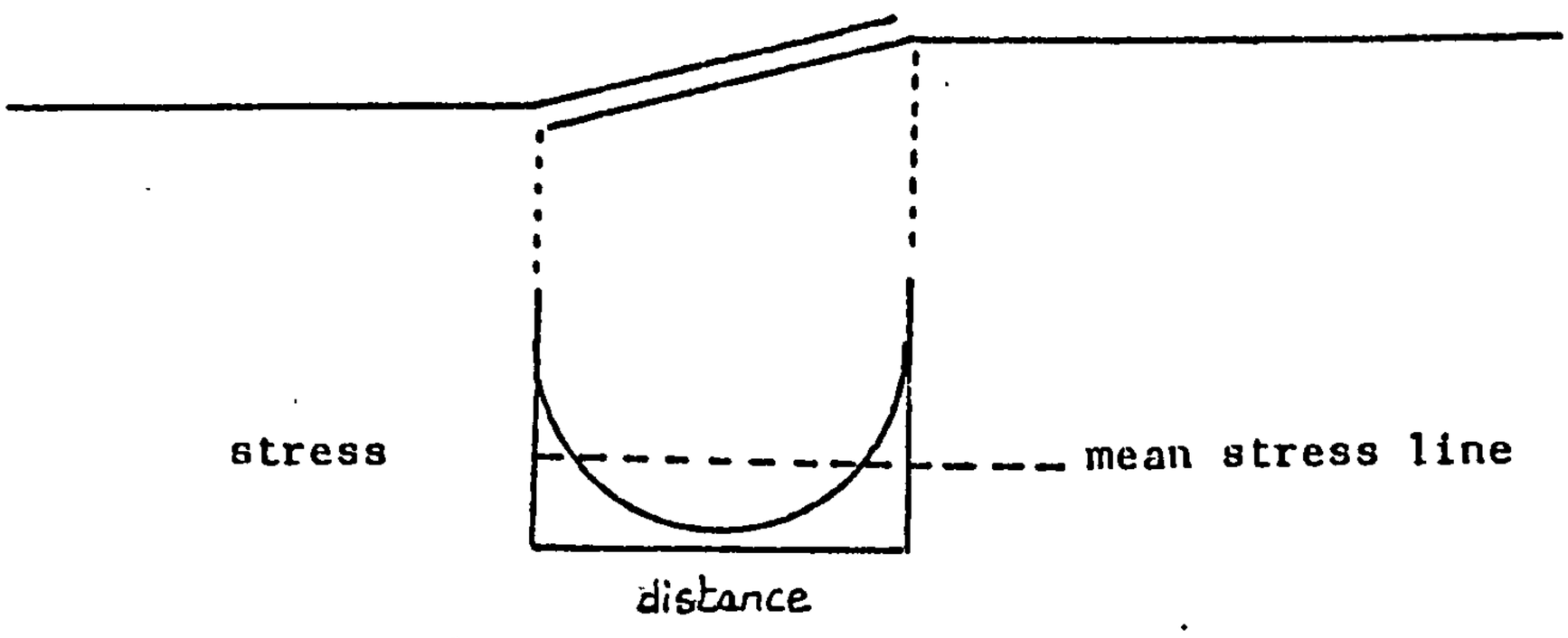


Fig.6
Distortion and stress in a lap shear joint

secondary stress, such as peeling or cleavage. Attempts to remove secondary stresses have led to redesigning the joint. An improved version is the double lap joint (fig.7). The single lap shear joint is however still widely used.

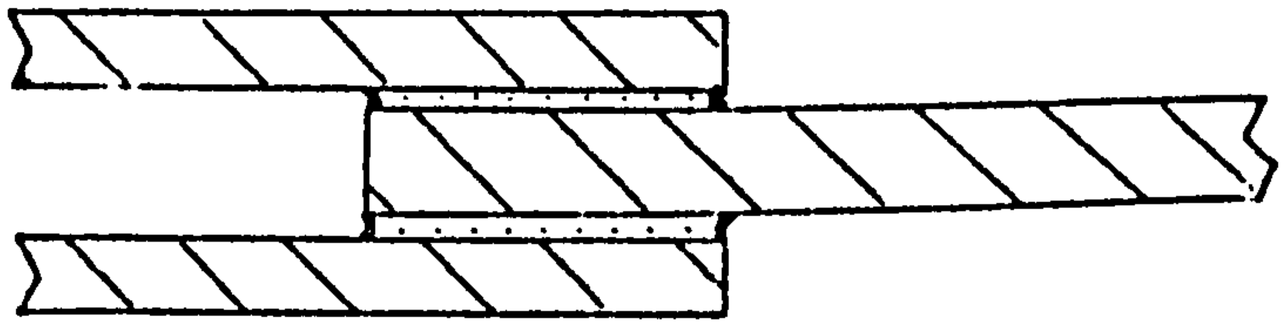


Fig.7 Double lap shear joint

In cleavage loading, the whole of the adhesive is not under equal stress. In fact one side of the joint may be under great stress, while the other is under no load whatsoever. This type of joint is seldom used in testing.

In peel, stresses are confined to a very fine line at the edge of the joint. In this case most of the adhesive is under no load at a given time. Since the stress concentrations will be high, unless the adhesive is very flexible, failure will occur at comparatively low loads.

The tensile properties of the adhesive can be seen to be important. Adhesives with low moduli will give higher peel strengths but lower shear or direct tension strengths. Conversely, high modulus adhesives will give stronger lap shear strengths but lower peel strengths.

Testing conditions are known to affect the value of bond strengths. These include strain rate, temperature, and humidity. Depending on the type of adhesive and test, increasing the temperature will increase or decrease the bond strength. Increasing the temperature with some adhesives may raise them above the glass transition temperature, and thus lower the bond strength dramatically. Increasing the temperature in other cases may lead to a reduction in the number of stress concentrations and thus increase bond strengths.

The speed of testing also affects bond strengths. On the whole the higher the strain rate, the higher the bond strength. This is due to stress relaxation effects. At high strain rates molecules do not have time to flow past each other, dissipating some of the energy. This effect is particularly noticeable in polymers such as nylons.

Humidity is known to have a deleterious effect on bond strengths. In the case of glass reinforced composites, water is known to wick along the fibres breaking the glass to matrix bond.

1.4.5 Weak Boundary Layers.

It has been known for a long time that metal surfaces must be thoroughly degreased before successful bonding can occur. The fact that greases and oils can prevent adhesion is constantly made use of in cooking. Industrial polymers invariably contain a variety of additives to improve their processability. These include antioxidants, lubricants, slip agents, anti-blocking agents and other processing aids. Some of these are non-soluble in the polymer and migrate to the surface. Such materials can produce a region of low strength at the surface and are called Weak Boundary Layers. Bikerman (33) has suggested the following as being the sources of weak boundary layers:- (i) the medium in which the joint is formed, usually air, which is incompletely displaced by the adhesive, (ii) the adhesive - may contain a region of low strength in its surface, such as a lubricant, (iii) the adherend, (iv) air and adhesive, and (v) air and adherend, where heating may cause a weakly adhering oxide to form on the surface, (vi) adhesive and adherend - such as a reaction between brass and sulphur from a vulcanised rubber to produce a metal sulphide, which will not adhere, (vii) all three - where the adherend may catalyse the reaction between the adhesive and air. Bikerman then reasoned that the role of pretreatments lay in producing a strong surface by removing the weak boundary layer.

A chemically pure surface is not necessarily a strong surface. For instance, an aluminium surface covered with aluminium dust is chemically pure, but it is not strong. Before a good bond can be achieved the dust must be removed. Conversely, an aluminium oxide on the surface

of the aluminium is chemically an impurity, but depending on its method of preparation can be very strong. Bikerman and others (34) have suggested that the poor adhesion of polyethylene and PTFE are due solely to weak boundary layers. More recently however there have been doubts cast on the validity of these views (35). Nonetheless, weak boundary layers may be important and must not be ignored, especially in practical situations.

1.4.6 Pretreatments.

Pretreatments for polyethylene and PTFE have already been mentioned. It is common in industry to pretreat the surface prior to bonding for a wide variety of substrates. The methods used are many. These include solvent degreasing, solvent wipes, sanding, shot blasting, flaming, electrical discharges and treatment with various reagents. While none dispute the efficacy of pretreatments, there is much controversy over their mechanisms. This will be discussed in detail later.

1.5 Forces acting across the interface.

There has been much argument over which forces are responsible for adhesion. There is controversy between supporters of chemisorption and those who rely on van der Waals' forces to explain adhesion. Three different effects contribute to van der Waals' forces: (a) the interactions of permanent dipole moments, known as the Keesom effect, where the mutual potential energy of attraction between different molecules of dipole moment μ_1 and μ_2 is given by the equation:

$$V_{Keesom} = \frac{2}{3kT} \cdot \frac{\mu_1^2 \mu_2^2}{r^6}$$

where k is the Bolzmann constant; (b) the polarizing action of one molecule on another, known as the Debye effect. If the attractive

forces between molecules were due only to the Keesom effect, then increasing the temperature should lead to decreased attraction. This is at variance with experimental data. The expression for mutual attraction between two different molecules is given by the expression:

$$V \text{ Debye} = \frac{a_1 \mu_1^2 + a_2 \mu_2^2}{r^6}$$

where a is the polarizability of a molecule; (c) the attraction of apolar atoms known as the London effect. The Debye effect does not explain the attraction between inert gases, which on a time average basis do not possess a dipole moment. London (36) suggested that an instantaneous picture of molecules be considered, where various electronic configurations would exist. Thus for very short periods of time, molecules would possess dipoles that would induce dipoles in neighbouring molecules. Thus attraction between the molecules would arise. For two molecules of polarizability a_1 and a_2, the expression for the attraction would be:

$$V \text{ London} = \frac{3h}{2} \cdot \frac{\nu_1 \nu_2}{\nu_1+\nu_2} \cdot \frac{a_1 a_2}{r^6}$$

where h is Planck's constant and ν_1 and ν_2 are characteristic frequencies.

Tabor (37) has calculated that for an organic adhesive with a surface energy of 30 ergs cm^{-2}, the force required to remove the adhesive from a metal surface in direct tension would be about 6×10^{18} dynes cm^{-2}. As these forces are not achieved in practice, Tabor suggested that it is enough to consider van der Waals' forces as sufficient. However, the calculation is based on the assumption of complete wetting of a planar surface. As has been stated earlier planar surfaces and complete wetting are difficult to achieve. It is quite possible

that comparatively few chemical links which are much stronger than van der Waals' forces, could account for the same force of attraction. It must however be born in mind that before chemisorption can occur, van der Waals' attraction must have taken place.

1.6 Type of Failure

There are three basic possible loci where failure can occur. It can occur at the interface between the adhesive and substrate, where it is known as adhesive or interfacial failure. It can occur in the bulk of the adhesive or the adherend, where it is termed cohesive or material failure respectively. It is possible for more than one type of failure to occur. Much of what is interfacial failure appears to be such to the naked eye. Quite often, microscopic examination reveals that some transference of material has occurred. Bikerman (33) has argued that true interfacial failure seldom occurs, since the attraction between two different molecules is greater than between molecules of the weaker material. This is based on the premise that interfacial attractions across the interface never deviate significantly from the relationship: $a_{12} = (a_{11} \cdot a_{22})^{\frac{1}{2}}$, where a_{12} is the attraction between phases 1 and 2, and a_{11} and a_{22} are the attractions between the like molecules of phases 1 and 2. Where apparent interfacial failure occurs, this must be due to very thin weak boundary layers. Although there has been support for Bikerman (34), there are those who believe that true interfacial failure can and does occur. Huntsberger (38) argues that the disparities in the sizes of atoms or molecular groups, non random distributions at interfaces, differences in ionization potentials and especially differences in polarity act to reduce the interactions between dissimilar molecules. Consequently a better generalization for the interactions across an interface is probably:

$a_{12} < (a_{11} \cdot a_{22})^{\frac{1}{2}}$. Good (39) introduced the parameter $\mathbb{0}$, to express the interaction as: $a_{12} = \mathbb{0}(a_{11} \cdot a_{22})^{\frac{1}{2}}$, and Huntsberger used the parameter θ to establish a criterion for the interfacial separation, $\mathbb{0}(F_a/F_b)^{\frac{1}{2}} < 1$, where F_a is the surface free energy of the substrate and F_b, the surface free energy of the adhesive. Using the data of Good and Co-workers for interactions between water and aliphatic hydrocarbons, he showed that for water - decane and water - liquid petroleum, the failure would be interfacial since $\mathbb{0}$ for the system was 0.95 and 0.77 respectively. Further experimental verification (40) was obtained for a low molecular weight polyisobutylene polymer adhered to an alkyd resin. Interferometry was used to establish that failure occurred at -1.3 ± 3.3 nm from the interface, and since failure was unlikely at the crosslinked alkyd resin, the failure was probably at the interface.

1.7 Methods of examining treated surfaces.

There is a variety of methods available for studying the effect of treatment on surfaces. Some of these methods such as LEED are more suitable for metal rather than polymeric substrates. The methods described below are applicable to polymers. The methods can perhaps be divided into "scientific" and "technological". In industry the reasons for investigating treated surfaces are often from the quality control point of view. Such tests must be simple and easy to use and must give clear-cut results. A variety of methods has been devised, and many have been found to work by trial and error. The results can often be applied to only one polymer. These methods seldom give any idea of changes in surface chemistry or geometry.

1.7.1 "Technological" methods.

These can be divided into the following groups:- (1) those tests, which measure the wettability of the surface, (2) tests which measure

the adhesion of contact adhesive tapes, and (3) tests which measure the adherence of inks or adhesives.

1.7.1.1 Tests measuring the Wettability of Surfaces.

These tests can be divided into contact angle measuring tests, and tests where the behaviour of liquid films on surfaces is observed. It has been mentioned earlier that contact angles can be a useful measure of the surface energy and thus the polarity of a surface. They can also be used to give an idea of surface roughness. Contact angles are a popular means of looking at the effects of surface treatment. There are several ways of measuring contact angles. A variety of liquids can be used, provided that they are free from surface active agents. The most commonly used liquid appears to be water.

A common method used for contact angles involves placing a drop of liquid on the surface. The drop is then illuminated and a magnified image is projected onto a screen. A tangent is then drawn and the contact angle is measured. An advantage of this method is that photographs of the image can be taken, and measurements made later. A disadvantage is that there can be problems with focussing the image.

In a different method a goniometer eyepiece is used to look at the drop. The eyepiece possesses crosswires, which can be aligned with the base of the drop and then with the tangent. The difference in readings gives the contact angle. The method is simple to use and the results are reproducible to $\pm 2^{o}$ (41). A disadvantage is that too many readings can lead to eye strain. Some workers have enclosed the drop in draught proof cells. (42)

The tilting table test avoids eye strain. Here a measured drop of

water is placed on the sample, which is on the tilting table. The table is then rotated slowly at a uniform rate, until the drop begins to move. The angle of tilt is the contact angle. (43) The disadvantages are that the contact angle is dependent on the rate of tilt and size of drop. Also the results are not readily reproducible. (41)
A somewhat different approach is that of Fort and Patterson. (44) They constructed a goniometer as in fig 8. The mode of operation is simple. A light is shone at the drop and the reflected light is observed. The light source is rotated until the light is no longer reflected. This gives the contact angle. Advantages of this method are ease of construction of goniometer, simple operation and reproducible results. Disadvantages are the need to work in a dark area and the impossibility of measuring angles greater than 90^{o}.

The other methods of measuring wettability involve brushing with or dipping the sample into a liquid. The subsequent behaviour of the liquid film gives an idea of the effect of treatment.
Perhaps the simplest is the nitroethane test. Here nitroethane containing a suitable dye is brushed onto the treated surface. If the film breaks up into droplets, treatment is considered inadequate for bonding. This test is very simple to use.
A test similar to it is the water dip test. Here the treated sample is dipped into cold water. If the water film formed persists for more than 30 seconds, the surface is considered suitable for bonding.
More complicated tests are the wetting tension tests. A range of liquid mixtures of different surface tensions is used. The highest surface tension mixture which does not break up into droplets within two seconds of placing the sample is determined. If this is 38 dynes

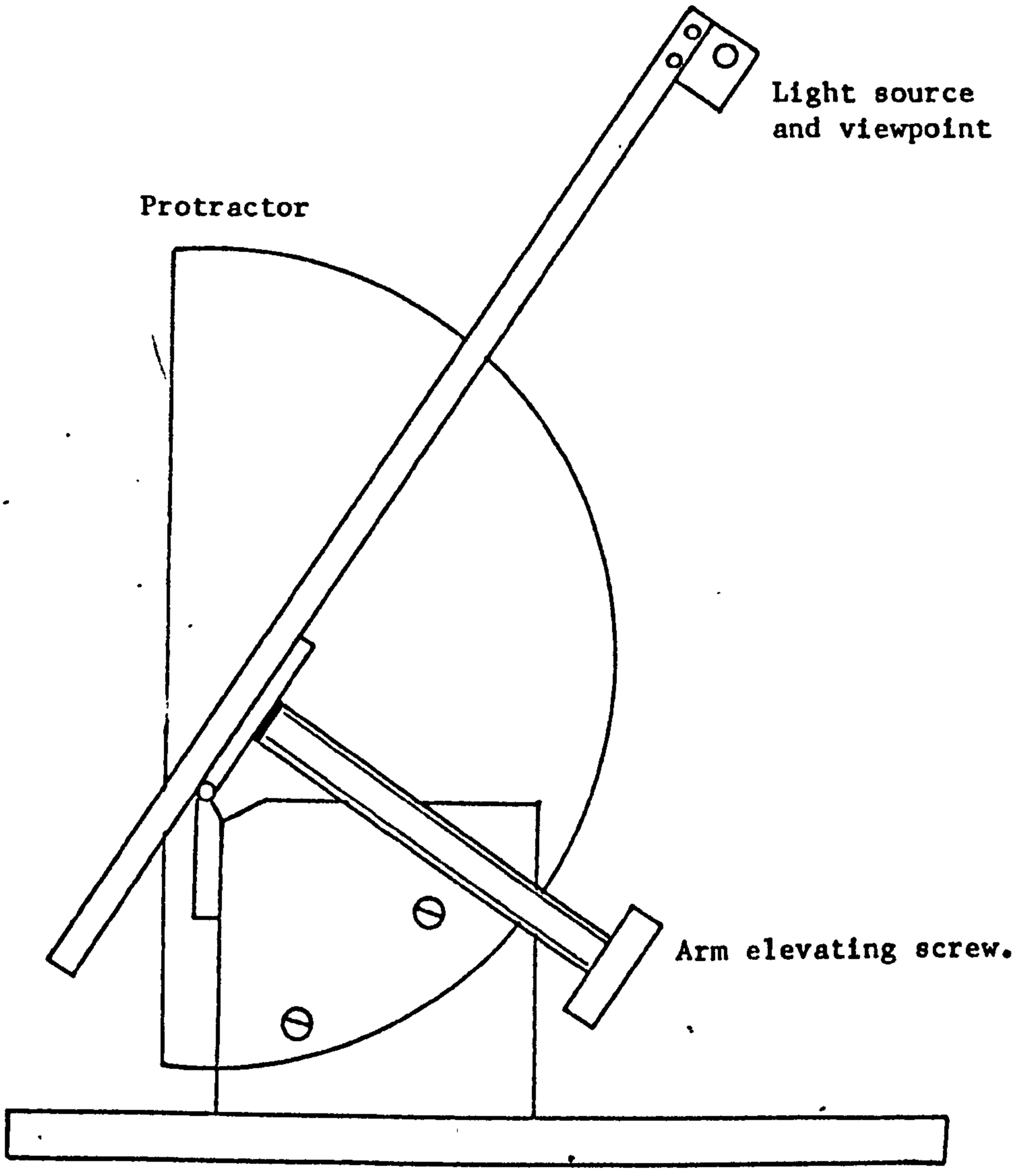


Fig.8. Diagram of contact angle apparatus of Fort and Patterson (44).

cm^{-1} or more the surface is thought to be suitable for printing or bonding. Errors can arise if the liquid mixtures are not suitably stored or allowed to become contaminated.

1.7.1.2 Tape Adhesion Tests

This type of test is exemplified by method 310F in BS.2784. In this test a standardized tape is used. It must first be tested by bonding to a standard metal surface and the peel strength found. Only if this falls within specified limits may the tape be used. The tape is then applied to the treated surface under given pressure. The peel strength is then determined. If this is above a predetermined level the surface is suitable for printing or bonding.

1.7.1.3 Ink Adherence Tests.

One method of measuring ink adherence is the "Scotch Tape" test. This involves applying a controlled thickness of ink. Tape is then applied to the ink and peeled off. If only a small quantity of ink is removed then the surface is suitable for printing. This is a very simple test to perform. In spite of being widely criticized it is extensively used.

Another method uses printing ink itself as the adhesive. The ink is applied between the surface to be tested and another surface. The assembly is stored for several hours at an elevated temperature and then peeled. The main disadvantage of this test is the length of time needed to complete it.

Related to these ink adhesion tests are the various tests which measure bond strength between surfaces and adhesives. These have been mentioned earlier.

1.7.2 "Scientific" Methods.

The "technological" methods are not the only ones used by industry, even though they are used widely on the shop floor. More scientific methods are also used to gain an insight into the fundamental changes which are caused by pretreatments.

1.7.2.1 Microscopy.

Microscopy is used for studying physical changes. For this purpose both optical and electron microscopy are utilized. The advantage of electron microscopy lies in much higher resolution. A microscope can at best discriminate between two point objects more than $0.6\lambda/\sin\theta$ apart, where λ is the wavelength of illuminating radiation and θ is the aperture angle of the cone of radiation that participates in image formation. For green light, in the case of a light microscope, λ = 5,000nm, even if all the radiation is used, making $\sin\theta = 1$. The smallest resolvable distance is about 2,000nm. For a transmission electron microscope in the 50-100kV electron range, λ is in the range 0.053-0.037nm. So even if the cone of radiation angle is 0.01 radians, the least resolvable distance is very low, about 3nm. Also the maximum useful magnification of a light microscope is 2,000 times. That of an electron microscope is about 1,000,000. Further advantages include a much better depth of focus, about 300 times higher. In general a compound light microscope consists of a light source, a condenser, an objective lens, and an eyepiece, which can readily be replaced by a recording device. It is thus cheap and easy to use. In its simplest form a transmission electron microscope consists of a source supplying a beam of electrons of uniform velocity, a condenser lens, a specimen stage, an objective lens, a projector lens and a fluorescent screen on which the final image is observed. The

screen can be replaced with a photographic plate, if permanent records are required. Since electrons are scattered even by air, the microscope must be evacuated (10^{-4}torr.) The thickness of samples is important, since with thicker materials multiple scattering of electrons by matter destroys the contrast in the image. Also energy transferred by inelastic collisions can become large enough to destroy the specimen.

Surfaces of materials too thick to be used directly can be examined by preparing replicas of the surface. These are usually made by applying a solution of collodion in acetone to the surface, allowing to dry and stripping off. The replica is then coated with carbon. Since materials of low mass density do not produce appreciably greater scattering than the film they are mounted on, it becomes necessary to deposit an extremely thin layer of metal at an oblique angle. Thus any projections above the surface receive a heavier deposit of metal on the side facing the metal evaporating source, and cast a shadow in which no metal is deposited. This metal shadowing produces a topographical representation of the specimen surface. Scattering occurs from the shadowed areas which will appear light, while non-shadowed areas will appear dark on photographic plates. With replicas a problem arises of the limitations of surface reproduction. Not only must the surface structure be related to internal structure, but care must be taken to recognise artifacts due to the replication process itself. The process of replication is time consuming. Much of this work can be obviated by using a scanning electron microscope. The sample is mounted on a circular metal slab, using a conducting adhesive. All the surface requires is a thin conducting layer, usually of metal, for examination. The main disadvantages of

SEM over TEM are the higher cost and a reduced resolving power. Current SEM resolutions are in the order of 15nm. Depth of focus is 300 to 500 times that of an optical microscope for the same magnification.

1.7.2.2 Infra Red Absorption Spectroscopy

This is a technique that can enable the chemistry of material to be deduced. The basis of this method lies in the interaction of infra red electromagnetic radiation with matter. This results in the absorption of certain wavelengths, the energy of which corresponds to the energy of transition between various states of molecules, or groups of atoms in a molecule. In the spectrum produced, the absorption intensity is recorded as a function of wavelength. Specific groups of atoms in a molecule give rise to characteristic absorption bands whose wavelengths fall within a definite range, regardless of the composition of the rest of the molecule. This makes it possible to determine the functional groups present in the sample analysed.

As the intensity of absorption is a measure of the concentration, infra red spectra may be used in qualitative analysis. (45)

Infra red absorption spectra can be obtained by three methods. The most common of these is direct transmission, in which the fraction of radiation that is transmitted is measured. Thin films may be used directly. The main disadvantage is that the surface concentration of functional groups may be very small compared with the bulk. Thus, these groups may not show up in the spectra. To get round this it is possible to use several layers of thin treated films (16), or to scrape the surface of the film with KBr powder using wire wool, and pressing the scrapings into a disc. The disadvantage of the latter method is that contamination by dust can occur, since abrasion of the film causes static.

Attenuated total reflectance (ATR) spectroscopy is used in cases, where the sample is too thick for direct transmission work. The sample is firmly pressed against the back of a small prism or hemicylinder made from a high refractive index material (eg KRS-5, - a mixture of thallium bromide and iodide). Good optical contact between prism and sample is essential. Where this cannot be achieved, the interface may be filled with a high refractive index liquid such as methylene chloride. The resulting spectrum will however have bands due to the liquid superimposed on it. The angle of incident radiation at the boundary between the sample and optical material is wider than critical. Part of the radiation penetrates beneath the reflecting surface of the material under analysis. Internal reflection occurs, and at the ratios of the refractive indices of both materials, the reflected light returns to the reflecting surface modified by absorption in the sample. If more than one internal reflection takes place, the method is termed multiple internal reflection spectroscopy (MIR). Spectra obtained by this method resemble transmission spectra. Since in ATR the beam of radiation penetrates to only its own wavelength in the sample (46), the thickness of sample beyond this depth of penetration is of no significance.

The last method, that of reflectance is seldom used.

1.7.2.3 Talysurfing

Another method of observing surface geometry is to use a stylus instrument such as a Talysurf. The Talysurf comprises: (i) a measuring head comprising a stylus for motion perpendicular to the test surface, and an indicating device coupled to the stylus. The indicating devices can be mechanical, optical or pneumatic. The stylus itself is in the form of a four sided 90^{o} diamond pyramid with

a slightly rounded tip, about 0.0254mm wide, which bears on the surface with a force of about 100 milligrams; (ii) a means of traversing the measuring head across the surface. Both manual and electrical means are used; (iii) means of providing a datum line against which the up and down movement of the surface can be measured; (iv) a means of providing a graphical or numeric representation of the cross-section of the surface. The numeric representation most often used is the centre-line-average (CLA) value. This is a numerical assessment of the average height of irregularities constituting the surface texture, expressed in microns or microinches. In most modern machines this is done automatically by averaging the results of several consecutive lengths. While the method is widely used for metallic surfaces, it has seldom been used for polymers.

1.7.2.4 X-Ray Fluorescence.

In this method specimens are subjected to an intense X-ray beam, which causes the elements in the specimen to emit their characteristic X-ray spectra (i.e. fluoresce). The lines of the spectra are diffracted at various angles by a single crystal plate in a manner analogous to a diffraction grating. Elements can be identified by the wavelength of their special lines, which vary in a regular manner with atomic number. Concentration can be determined from the intensities of the lines. The method can be used for concentrations greater than 0.01%. The disadvantage of this method is that the sensitivity and accuracy decrease rapidly for the low atomic number elements, sulphur and below, because of various problems associated with long wavelength X-rays generated by these elements.

1.7.2.5 Secondary Ion Mass Spectrometry (SIMS)

In this technique the sample is bombarded with a 5-20eV beam of primary ions. This sputters off the surface layers of the sample producing a variety of secondary species such as neutral atoms, photons, electrons, positive and negative ions. Mass spectrometric analysis of the positive and negative ions can provide chemical characterisation over the complete elemental range (47). Detectability is in the range 10^{-15} to 10^{-19}gm.

Ion bombardment can produce positive ions by either kinetic or chemical means. A primary ion of 5-20KeV can transfer its energy on striking a surface to the sample atoms. This initiates a collision cascade, which results in the ejection of sample atoms as well as excitation to metastable or ionized states. Any unbound electrons in the sample will have a much higher velocity than solid state ions have, and will be neutralized before they can escape into the vacuum. However an atom can escape from the surface as a neutral particle while at the same time being in a metastable state. Such an atom can eject an Auger electron in the vacuum above the surface, and thus become an ion capable of detection by the mass spectrometer. This is in essence the kinetic process.

The chemical process depends on the presence of one or more chemically reactive species in the sample to reduce the number of conduction band electrons available for reneutralization of ions produced in the solid. With the reduction of neutralization events, more ions produced can escape the surface. When chemical ionization predominates, the majority of ions are produced in the outer 50nm of surface.

1.7.2.6 X-ray photoelectron spectroscopy (XPS)

Originally designated as electron spectroscopy for chemical analysis (ESCA), it was developed by Prof. K. Siegbahn. In this technique, the sample in a high vacuum is irradiated with monochromatic X-rays of known energy, and the energy of the photoelectrons emitted is recorded. The apparatus is shown in a schematic form in fig.9. Electrons from a heated tungsten wire are accelerated to the anode. The radiation resulting from collisions is emitted and passes through a window onto the sample where it induces photoelectrons. These are deflected in the electrostatic analyser, double focussed and counted by an electron multiplier. The system works under a vacuum of 10^{-7} to 10^{-10} torr. It is possible to connect the machine to a computer, which can time average the results over several runs as means of increasing sensitivity. The output of the machine can be by oscilloscope or more often by means of a chart recorder.

In the photoionization process the X-rays liberate electrons in the various orbitals of the sample. Depending on the energy of the X-ray beam the electrons are either absorbed into the valence band near the Fermi level or leave the atom as free electrons with a kinetic energy of E_k. Now $E_k = E_x - E_i$, where E_x is the energy of the X-ray beam and E_i is the ionization energy of the orbital. These energies are characteristic of a given element and are sensitive to the electronic environment of the atom. {Thus, while for a given core level of an element, the absolute binding energy is characteristic of that element, differences in electronic environment give rise to a small range of binding energies, called shifts, often characteristic of particular features (48) }. The binding energies of core electrons are affected by valence electrons and thus the chemical environment of the atom.

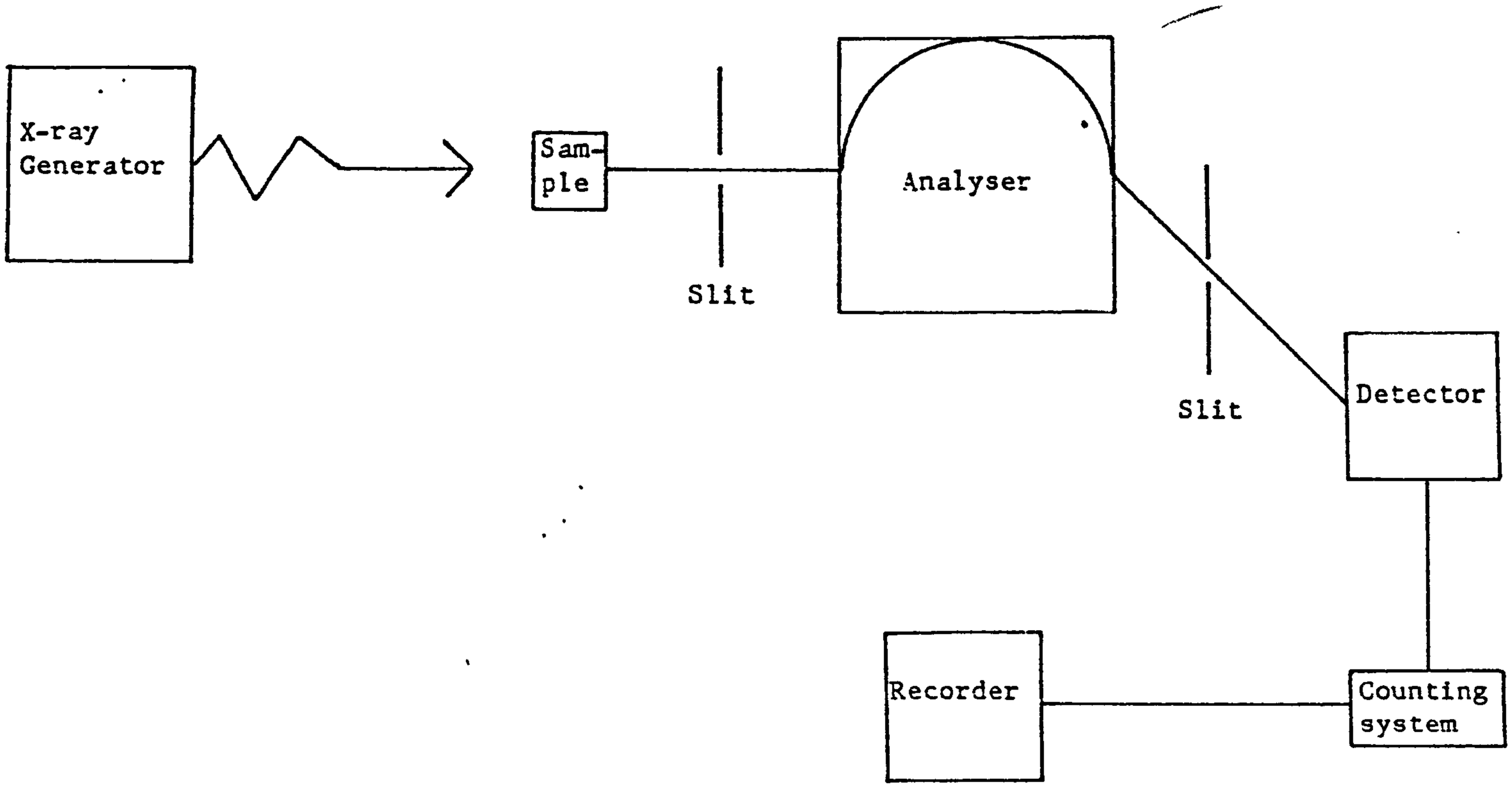


Fig.9. Schematic representation of an XPS apparatus.

The attraction of the nucleus for a core electron is somewhat diminished by the presence of the outer electrons. If one of the valence electrons is removed, the amount of shielding is decreased, the effective nuclear charge on the core electrons is increased, thus increasing the binding energy. This is made use of to give information about the type of functional groups present.

1.8 Theories of Adhesion

1.8.1 Early Work.

As a result of the work of McBain and his co-workers (49, 50) adhesion was considered to be the result of two phenomena: (i) adhesion due to mechanical keying, where the adhesive flowed round fibres or into crevices of the substrate; and (ii) what was termed specific adhesion. Specific adhesion was thought to be due to Van der Waals' forces and/or chemical attraction. Van Roy (51) considered that the specific theory of adhesion was inadequate by itself. As a result of his research he noted that strong bonds were formed if there was a similarity in polarity between adhesive and adherend. Weyl (52) proposed that adhesion was too complex a phenomenon to be due to one cause. He rejected the influence of mechanical bonding in most cases, and suggested that adhesion resulted from chemical forces, with Van der Waals' forces being the first step in bond formation. He said that many examples of adhesion could be explained by means of a chemical equation. He also pointed out that surface structures were very different from the bulk, and drew attention to the fact that good wetting was needed for bonding and mentioned its relationship to contact angles. McLaren and Seiler (53) pointed out the need for polarity in adhesives if these were to wet surfaces. De Bruyne (54) observed that compatibility of adhesive and adherend was needed for

good bonds. This is known as the De Bruyne rule, which states that strong joints can only be made to polar surfaces with polar adhesives and to non-polar surfaces with non-polar adhesives. He later suggested that physical intermolecular forces would form an adequate basis for adhesion (55). Bikerman (56) while admitting that polar forces could be useful in bringing an adhesive into contact with a substrate denied their contribution to resisting bond failure. He ascribed the ultimate strength of joints to the rheological properties of the adhesive-adherend system.

Deryagin (57) as a result of peeling PVC from glass at different pressures of argon noticed that condenser discharge energy increased with decreasing pressure of gas. This led him to suggest that the adhesive-adherend act like a capacitor system, and that adhesion is due to the electrostatic attraction between two different surfaces. The mechanical theory, which had begun to lose ground was reinforced by the work of Borroff and Wake (58) who showed that the bond strength between cotton and various rubber cements was unaffected by the surface treatments of the cotton.

Tabor (37) calculated that for a solid completely wetted by a liquid hydrocarbon, the force resisting separation would be 154MN m^{-2} even if only Van der Waals' forces were acting. He suggested that the discrepancy between theoretical and observed results was due to the vast difference between theoretical and real strengths of solids, as well as to the existence of stress concentrations in the adhesive itself or at the adhesive meniscus.

Bikerman (56) compared the importance of 'molecular' forces with 'rheological' forces during the different stages of making and breaking joints. Adhesives were applied in liquid form and the degree of

contact depended on the wetting power of the liquid. This wetting power according to Bikerman was a molecular phenomenon. The resistance to be overcome in trying to separate two solids joined by a liquid adhesive was a function of viscosity, and therefore a rheological phenomenon. Similarly, on setting of the adhesive the breaking forces would depend on the mechanical properties and would be therefore a purely rheological phenomenon.

Voyutskii and his co-workers (59-61) studied the various factors needed for autohesion to occur in rubbers. They found that coalescence of two samples in close contact was a function of time; pressure was only needed to ensure that the surfaces came into close contact; smooth surfaces needed less pressure; softeners and plasticisers promoted autohesion and an increase in temperature decreased the forces inhibiting autohesion. Fillers were found to inhibit autohesion. The mechanism of autohesion was explained as being a diffusion process in which segments of chains diffused across the interface and intermingled, leading to the disappearance of the boundary. The presence of polar groups was found to cause an increase in activation energy of autohesion and this was used to explain the lack of autohesion in cellulose and its esters.

Witt (62) in 1947, working on coupling agents for glass fibres found that the agents contained functional groups, which reacted with groups present in the surface of the glass. The coupling agents also contained groups which could co-polymerise with the laminating resin, an unsaturated polyester resin.

Rossman (16) studied the effect of glow discharge at reduced pressure and Tesla coil discharge on polyethylene film by means of infra-red transmission spectroscopy. He found that there was an increase in

unsaturated C=C bonds and carbonyl groups. He suggested that improvements in bonding caused by the treatment was due to oxidation of the surface of the polymer.

Wechsberg and Webber (63) studied the effect of altering the variables during corona discharge treatment of polyethylene. They found that peel strength increased with increase in the voltage applied. It decreased with an increase in film speed and with increase in the gap width. Slip additives strongly affected the peel strength, oleamide raising it and ethylene bis stearamide reducing it.

Voyutskii (64, 65) as a result of further work developed a new theory of adhesion. In this theory, both the adhesion of high polymers to each other and autohesion consist of diffusion of chains of molecules or sections of them from one polymer to the other. This inter diffusion is determined by the polarity relationships of the polymers.

Systematic studies of W.A.Zisman and co-workers of the equilibrium contact angles of a variety of pure liquids on low energy surfaces revealed interesting results. It was found that a rectilinear relationship was empirically established between the cosine of the contact angle, θ, and the surface tension, γ_{lv} for each homologous series of organic liquids. This led to the development of the critical surface tension of wetting, γc, (66) for each homologous series as defined by the intercept of the horizontal line $\cos \theta = 1$ with the extrapolated straight line plot of $\cos \theta$ against γ_{lv} (see fig.10). A liquid with a surface tension lower than γc

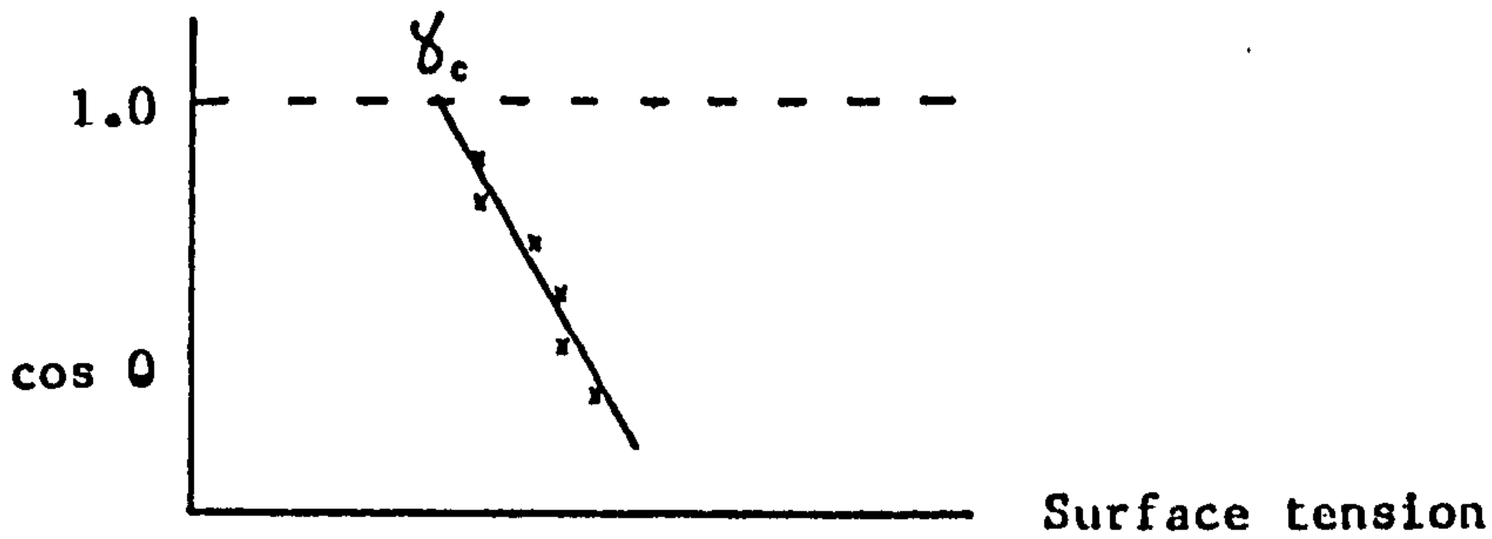


Fig.10. Relation between cos θ and surface tension.

would be expected to spread on the surface of the solid. Zisman's studies of wetting of various types of hydrocarbon surface showed that γc is susceptible to changes in packing of groups in the surface studied as well as to the chemical nature of the groups themselves. Thus in hydrocarbons there is an increase in 10 dynes / cm in γc when changing from methyl $\leftarrow CH_3 \rightarrow$ to methylene $\leftarrow CH_2 \rightarrow$ groups. Similarly replacing one hydrogen atom per repeat unit in polyethylene by chlorine gives an increase in γc from 31 to 39 dynes/cm. Thus the contact angle, which is dependent on γc has much significance in technological aspects of wetting and adhesion. Thus, Zisman pointed out that the increase in contact angle observed by de Bruyne (67) when treating polyethylene with chromic acid could only be due to chemical modification of that surface.

The need for wetting to occur before successful bonding could take place was shown by Huntsberger (68) who observed the effect of temperature on joint strengths, and Sharpe and Schonhorn (69) who showed that although epoxy adhesive-polyethylene joints had poor bond strengths; when polyethylene was melted onto solidified epoxy, a substantial increase in bond strength was obtained. The explanation given was that epoxy adhesive would not spread on low energy polyethylene; however, polyethylene, when molten could spread on the much higher energy epoxy; viscosity could not be a sufficient answer. Their other

results were generalised as follows:- every liquid having a low specific surface free energy would always spread freely on a specularly smooth, clean surface at ordinary temperatures, if its viscosity was low, unless the film adsorbed by the solid converted it into a low energy surface,having a critical surface tension less than the surface tension of the liquid. Because of the highly localised nature of forces between each solid surface and the molecules of each liqud, a monolayer was always sufficient to give the high energy surface the same wettability properties as a low energy surface having the same surface constitution.

Levine et al (70) obtained joint strengths for various polymers bonded with an epoxy adhesive. They found that there was a good relationship between the critical surface tensions of the polymers and the measured joint strengths.

Barbarisi (71) attempted to relate the bond strength of treated polyethylene to the work of adhesion, based on the equation $W = \gamma_{1v}$ (1 + cos 0). He measured the contact angle of an epoxide adhesive on polyethylene treated with chromic acid under various conditions. By plotting (1 + cos 0) against bond strength he obtained a straight line relationship. Brewis (72) has argued that the straight line relationship of Barbarisi was fortuitous. His criticisms were based on the low bond strengths obtained by Barbarisi and the fact that increasing treatment would alter other factors such as surface roughness.

1.8.2 Weak Boundary Layer Theory.

In 1959 J.J. Bikerman carried out a series of experiments on the bonding with polyethylene (73). He used polyethylene as the adhesive between two metal adherends. He then purified the polyethylene by dissolving it in toluene and reprecipitating it in acetone. When

the purified polyethylene was used as an adhesive, a considerable increase in bond strength was obtained. He then proceeded to add impurities to the polyethylene. In the case of oleic acid (74), concentrations greater than 0.1% had a deleterious effect on the bond strength. When ethyl palmitate was used, concentration of over 2% could be tolerated with no effect on the bond strength. When Bikerman added the ethyl palmitate to polyethylene containing 1% oleic acid, there was a marked improvement in bond strength (33). Bikerman explained these results by means of the Weak Boundary Layer theory : commercial (i.e. unpurified) polyethylene contains low molecular weight species, which migrate to the polymer surface, to which they are loosely attached. When an adhesive is applied, it bonds to this weak layer. Since this layer is weakly attached to the bulk, it and the adhesive can be readily removed. In the case of purified polyethylene, no such layer exists, and good bonding can be affected. However, when an impurity is added that will migrate to the surface, such as oleic acid, a weak boundary layer is formed giving rise to poor adhesion. Addition of ethyl palmitate allows the oleic acid to disperse within the bulk of the polyethylene effectively removing it from the surface, thus preventing the formation of a weak boundary layer. Having thus explained the reason for poor bonding, Bikerman proposed that the effectiveness of pretreatments was due to the removal of weak boundary layers.

The initial response to Bikerman's concept of weak boundary layers was unfavourable but the concept received a boost with the development by Schonhorn and Hansen (75) of "CASING", a new technique for the surface treatment of low energy polymers. "CASING" or cross-linking by means of activated species of inert gases, allows electronically excited

species of rare gases to impinge on the surface of the polymers. This treatment improves the bond strength, but does not appear to change the wettability of the surface, and ATR does not show any changes in surface chemistry. According to Schonhorn, the method owed its success to elimination of the weak boundary material composed of low molecular weight polymer molecules which were forced to the surface during recrystallization from the melt, by cross-linking it to the bulk material of the polymer. Evidence was presented for the existence of a cross-linked skin in "CASING" treated polyethylene and polytetrafluoroethylene.

Schonhorn presented further evidence in favour of the weak boundary layer. Schonhorn and Sharpe successfully formed strong adhesive joints, using a polychlorotrifluoroethylene-epoxy adhesive system (76). The surface energy of polychlorotrifluoroethylene is the same as that of polyethylene (c.32 dynes/cm) which does not form strong joints. Schonhorn and Sharpe concluded that this could only be explained by the fact that polyethylene possesses a weak boundary layer and polychlorotrifluoroethylene does not.

Further work by Schonhorn and Ryan (19), which involved melting polyethythene onto various substrates was used as further confirmation of the weak boundary layer theory. They melted polyethylene onto aluminium foil. When the foil was peeled off a non-bondable polyethylene surface resulted. When, however, the foil was dissolved off, a polyethylene surface with improved bonding characteristics was obtained. The explanation offered was that during the crystallization from the melt species contributing to the generation of weak boundary layers were rejected from the interface into the bulk, when in contact with a high energy surface. This resulted also in the formation of an

interfacial zone of high mechanical strength, which the authors called the transcrystalline region (TCR). Solvent extraction of the transcrystalline region showed no evidence of gel fraction. No evidence of surface oxidation was discovered by means of IR spectroscopy although a decrease in contact angle was observed. The reason for the high mechanical strength of this region was explained as due to considerable entanglement of polymer chains. Schonhorn also repeated the investigation with other metal substrates and with FEP (77) instead of polyethylene, with similar results. Again, a decrease in contact angles was obtained and improved adhesion occurred, and was explained in terms of the transcrystalline region. Decrease in contact angles was explained as due to greater density, due to higher crystallinity.

In further work, Schonhorn and Hara (78) used polyethylene as an adhesive for PTFE, FEP, and Nylon 6. They discovered that if the substrates were suitably treated then good bonding resulted.

This work reversed the conclusion of Schonhorn's previous work (79). The reason for poor bonding of polyethylene was due to the fact that polyethylene came in contact with its own vapour and thus produced a WBL. The effectiveness of the various pretreatments lay in the fact that either they physically removed eg by washing with chromic acid or by cross-linking it with the bulk, eg CASING.

The WBL theory became verypopular and found support with many. Armand and Atkins (80) treated polypropylene with chromic acid and found no evidence of chemical modification with IR spectroscopy. This, they concluded was evidence for the WBL theory.

K. Nakao (81) melted polyethylene onto aluminium and cooled the samples at various rates and temperatures. He found that peel strengths

increased with quenching, and deduced that this was due to micro-crystallization of polyethylene. Further evidence therefore of trans-crystalline region and thus more support for the WBL theory.

J. Cuthrell (42) measured the contact angles of various materials moulded against a variety of surfaces. He found that contact angles, which initially matched those of the moulds, changed with time. He also found that when successive layers of polymer were removed, the contact angle changed until a bulk equilbrium was reached. This work was interpreted as being in favour of the WBL theory.

Hurdis and Prescott (82) found the UV radiation would cross-link the surface of the polyethylene. Again, this was thought to favour the WBL theory.

1.8.3 Recent Work.

More recently, Blais and co-workers (83) etched polyolefins with chromic acid. The treated surfaces were characterised with contact angle measurements, peel strength determinations, SEM and IR spectroscopy. They noticed that although polyethylene showed changes in surface chemistry, polypropylene showed neither chemical nor topographical change, in spite of giving higher peel strengths. This, they concluded, could only be due to removal of a WBL by the treatment. Even though the WBL appeared to explain much, some workers did cast some doubt on its universal applicability. Brewis (35) treated polyethylene with chromic acid and then added a deliberate WBL and found only a slight decrease in bond strength.

Bright and Malpass (84) melted polyethylene against high energy substrates. They studied the effect of antioxidants and oxidizing agents. They found that bonding between polyethylene and high energy substrates could only occur if surface oxidation of the polyethylene

had occurred. As a result of further SEM studies, they suggested that surface roughness as well as oxidation should be considered essential to good bond formation.

Baszkin et al (9) treated polyethylene with sulphuric acid-potassium perchlorate mixtures. They then attempted to graft on maleic acid. Radioactive techniques were used to measure the number of polar groups. Characterisation by contact angles was also employed. It was found that the wettability of the surface was directly related to its chemical composition.

Fitchmun and Newman (85) found that for a given thermal history, the surface morphology was independent of mould surface. They discovered that melting polyethylene onto poly(ethylene terephthalate) could produce a transcrystalline region. Their results were in direct contrast to Schonhorn, who maintained that the TCR could only be produced by high energy substrates.

Sowell et al (86) exposed polyethylene and silicone rubber to an activated gas plasma. They used both argon and oxygen. Contact angles and bond strength determinations were used to follow the treatment. They found that treatment with argon did cause a decrease in contact angles. This was in direct contradiction to Schonhorn, who reported no change in contact angle. Sowell found that argon treated polyethylene contained free radicals, which remained "live" for at least 24 hours in argon, but which decayed within 5 minutes if exposed to air. Thus the authors suggested that in air, the main treatment mechanism is that of oxidation, although in argon it will be by cross-linking. However, on exposure to air, some surface oxidation will take place.

By 1972 many had already discounted the weak boundary layer theory. Amongst these was Sharpe (87) of Bell Labs. He suggested that it was

the mechanics of the composite system alone, independent of any material property change in the vicinity of the interface, which determined whether a joint failed in a thin layer of polyethylene near the interface. He suggested that the pretreatments caused a decrease in stress concentrations due to an increase in the toughness of the polyethylene surface region. Sharpe stated that stress concentrations were due to differences in moduli between adhesive and adherend. According to him, joint mechanics and energy interia were more relevant to the understanding of joint behaviour.

Some measure of support for this view came from Bikerman (88) who had expounded his original WBL theory into a rheological theory of which WBL concept became only a small part. Thus the strength of the joint was dependent on internal and external conditions such as thickness of adhesive layer and the method of testing.

Packham et al (89) melted polyethylene with and without antioxidant onto porous anodised and sealed aluminium. They found that for the porous substrate, adhesion was independent of oxidation, but for sealed aluminium surfaces, oxidation of the polymer was a prerequisite for good bonding.

Dwight and Riggs (90) repeated the work of Schonhorn and Ryan (77) melting fluoropolymers against gold. Examination of the surface with XPS showed the presence of a thin layer of polar, oxygen containing species. They suggested that this polar layer was more likely to give rise to the increased wettability and better bonding than the transcrystalline layer postulated by Schonhorn.

Blythe et al (91) examined the surfaces of polyethylene after Corona treatment in various gases by XPS. They found that oxidation of the surface occurred. They suggested that the source of oxygen was due to the

presence of water molecules adsorbed on the surface of the glass apparatus used.

1.9 Summary of the theories of adhesion.

1.9.1 Mechanical:

According to this theory, the adhesive interlocks in the crevices or pores of the substrate. It is generally believed that this mechanism may only apply in the case of porous materials such as paper, textiles and polymeric foams.

It does not explain the need for pretreating polyethylene. Treatments, such as chromic acid, do roughen the surface and improve bond strengths. However, mechanical roughening, although it increases the surface area, has very little effect on bond strength.

1.9.2 Electrostatic:

This theory postulates that the two surfaces in contact, act as the plates of a capacitor. Electrons are transferred from one material to the other, till the surfaces have opposite charges.

The fact that some adhesive joints have been found to be charged after rupture is cited as evidence. This explanation is not sufficient, since the process of rupture could lead to charge formation.

1.9.3 Diffusion:

This theory, based on the work of Voyutskii, states that the adhesive molecules diffuse into the substrate and thus lead to a disappearance of the interface. While none doubt the diffusion between identical or like rubbers, it is difficult to envisage the same process with two very dissimilar polymers.

Again this theory does not explain the need for pretreatments of polyethylene and polytetrafluoroethylene.

1.9.4 Adsorption:

According to this theory, adhesive molecules are adsorbed onto the substrate surface and held there by various forces of attraction. Attraction is thought to be mainly by van der Waals' forces, although chemisorption can occur in some cases.

Polyethylene is difficult to bond because the surface will not "wet". Pretreatments are needed to improve the wetting of the surface.

1.9.5 Weak Boundary Layer:

According to this theory, it is the presence of weakly held surface layers that prevents polyethylene, PTFE and certain other substrates from being readily bonded. Pretreatments remove this weak layer, either by dissolution or by cross-linking it into the bulk of material.

1.10 Aim of Present Work.

The aim of the present work was to increase the understanding of factors involved in the adhesion of low surface energy substrates. In particular the objective was to see whether poor adhesion of low energy substrates was due to weak boundary layers or due to other factors. A minor aim was to see if Sharpe's contention that the large modulus differences between epoxy adhesives and polyethylene substrates were the reason for poor bond strengths.

Most of the work carried out concerned two main topics:- (i) the existing pretreatments for polyethylene and to a lesser degree polypropylene, and (ii) two methods for treatment of polytetrafluoroethylene based on the findings of Dr. R.H. Dahm of Leicester Polytechnic. (Dr. Dahm noticed that polytetrafluoroethylene became black during certain electrochemical experiments). With the former, the pretreatments studied have been chromic acid etching of polyethylene and polypropylene; flame treatment of polyethylene; melting polyethylene against aluminium - this was extended to include extrusion of polyethylene onto aluminium and the use of polyethylene as the adhesive between aluminium adherends; aqueous persulphate and peroxide treatment of polyethylene; corona discharge treatment of polyethylene and polypropylene; and the effect of organic liquids or their vapours on polyethylene and polypropylene. The new methods of pretreatments of polytetrafluoroethylene involved attack by electrochemically generated anions and direct contact with polarised electrodes.

The main techniques that were used to study the changes caused to the

surfaces by pretreatments were:-

(a) joint strength determinations using single lap shear joints;

(b) contact angle measurements by means of goniometer eyepiece fitted to a travelling microscope;

(c) attenuated total reflectance infra-red spectroscopy (ATR) using a KRS-5 crystal giving 9 fold reflectance;

(d) X-ray photoelectron spectroscopy (XPS) to examine chemical changes at the surface. This is probably the earliest work on polyethylene pretreatments where XPS has been used to study the surface. The actual work involved in using the spectrophotometer was carried out by Dr. D. Briggs of ICI Corporate Laboratory.

(e) Changes in surface topography were studied by means of scanning electron microscopy and talysurfing.

A comparison was made of the shear strengths obtained using "Alkathene" WJG47 and two ethylene-vinyl acetate copolymers to check the validity of Sharpe's contention.

2. Experimental.

2.1 Materials.

"Alkathene" WJG47 is a low density polyethylene with a melt flow index of 2. Additive free blown film (thickness - 0.125mm) was used.

"Alkathene" WJG11 is the same polymer as "Alkathene" WJG47 but contains 200ppm of antioxidant (2,6-ditertiary-p-butyl cresol). Blown film of thickness - 0.125mm was used. "Alkathene" WNC71 is also a low density polyethylene but has an MFI of 7. Additive free material and material containing two different loadings of "Topanol" OC anti-oxidant (2,6 -di-tertiary butyl-p-cresol) was used. "Propathene" HF20, is a polypropylene homopolymer with an MFI of 3. Polymer containing no additives was pressed into thin films (thickness - 0.125mm) for 5 min. at 175°C between two films of poly(ethylene terephthalate) which had been extracted with trichloroethylene.

Two ethylene-vinyl acetate copolymers were used. A14271 contains 15% vinyl acetate by weight and has an MFI of 8. (thickness - 0.1mm). The other copolymer (24-03) contained 24% by weight of vinyl acetate.

The polytetrafluoroethylene used was mainly a skived film of "Fluon" G163 (thickness - 0.25mm). Some initial experiments were carried out using a bronze filled grade ("Fluon" VB60) containing 27% by volume of bronze (thickness - 0.75mm). All these polymers were kindly provided by Plastics Division ICI Ltd.

"Rigidex" 50 is a high density polyethylene with an MFI of 5. Additive free granules were pressed into thin films (thickness - 0.125mm) between sheets of poly(ethylene terephthalate). The material was supplied by BP Chemicals.

The adhesive used was an epoxide system made by Ciba Geigy Ltd.

"Araldite" AV100 is an epoxy resin based on Bisphenol A. "Araldite" HV100, a polyaminoamide accelerated with a tertiary amine, is the appropriate hardener and was used in a ratio of 1:1 by weight with the resin. Both resin and hardener contain thixotropic agents.

The aluminium adherends used in joint strength determinations were cut from extruded bar obtained from Alcan Ltd.

2.2 Pretreatments

2.2.1 Polyolefin Pretreatments

2.2.1.1 Chromic and sulphuric acids.

The basic chromic acid mixture was made up as follows: potassium dichromate (7 parts by weight), distilled water (12 pbw) and concentrated sulphuric acid (150 pbw). Polyolefin films were immersed in the acid for the conditions detailed later. The films were washed with agitation in 12 changes of distilled water for 15 minutes or overnight. The films were then dried under vacuum. A similar procedure was used for concentrated sulphuric acid treated films.

For certain experiments, the quantity of potassium dichromate used was decreased, but the other components were kept in their original ratios.

A different formulation of chromic acid was also used. This involved replacing sulphuric acid with the same weight of glacial acetic acid, and substituting chromium oxide ($Cr\ O_3$) for potassium dichromate, adjusting the weight to keep the chromium concentration constant. For some experiments the quantity of chromium oxide was increased fourfold. Because of the unpleasant nature of acetic acid, the acid and polyolefin films were kept in a reaction flask and the mixture stirred vigorously to ensure treatment on both sides.

Modification of Chromic Acid Treated Polyethylene.

1. Sodium Hydroxide Treatment.

Chromic acid treated films were subjected to aqueous 2M sodium hydroxide for various lengths of time. The films were then washed with distilled water and dried under vacuum. Then, the films were submitted to IR spectroscopy.

2. Hydrochloric Acid Treatment.

Films treated with sodium hydroxide solution were immersed in 2M hydrochloric acid. The films were then washed with distilled water, dried under vacuum and submitted to IR spectroscopy.

3. Treatment with Diazomethane

3.1 Preparation of Diazomethane.

The method used by Fieser and Fieser (92) was followed. Potassium hydroxide (5 gm) was dissolved in water (8 ml) in a 100 ml flask. Diazald (p - Tolysulphonylmethylnitrosoamide) (21.4 gm) was dissolved in previously dried diethyl ether (130 ml). The ethereal Diazald solution was added dropwise over 25 minutes to the potassium hydroxide solution via a dropping funnel. The gas evolved was collected in ether. When the dropping funnel was empty, dry diethyl ether was added, until a clear distillate was obtained.

3.2 Treatment

Chromic acid treated films were placed in the ethereal diazomethane solution. A glass covered magnetic stirrer was added and the flask was stoppered with a drying tube. The flask contents were left to stir for 24 hours. Then the films were removed, washed several times with clean dry ether and dried under vacuum. Then the films were submitted to IR analysis.

4. Treatment with 2,4 - Dinitrophenylhydrazine reagent

4.1 Preparation of Reagent.

The reagent was prepared by the method employed by Kato (93).

2,4 - dinitrophenylhydrazine (1 gm), hydrochloric acid (5 ml), distilled water (5 ml) and ethyl alcohol (100 ml) were mixed together. This reagent was always prepared just prior to use.

4.2 Treatment with Reagent

Chromic acid treated films were immersed in the reagent for 5 minutes. The films were then repeatedly washed with ethyl alcohol and dried under vacuum. The films were then subjected to IR analysis.

A blank, using untreated polyethylene, was run. Common ketones, such as acetone, were also treated with the reagent. Spectra of the products were compared with the chromic acid treated polyethylene.

5. Reduction of Treated Surface

The object was to try to reduce the treated surface to the untreated form and see if it behaved as an untreated surface.

The initial stage involved stirring the chromic acid treated polyethylene with lithium aluminium hydride (3.5 gm) in dried ether (100 ml). The mixture was kept in a round bottomed flask fitted with a reflux condenser and a calcium chloride drying tube. This treatment was continued for various lengths of time.

The films were removed and washed with dry ether, ethyl acetate and then vacuum dried.

Next, the films were placed in freshly distilled thionyl chloride. The films were stirred in the liquid while it was allowed to reflux for 3 hours.

Then the excess thionyl chloride was removed on a rota-evaporator.

The films were then washed with dry diethyl ether.

Next, the films were treated with a solution of superhydride in THF for 12 hours at room temperature, with constant shaking. The films were then washed with several changes of dried THF.

The films were then subjected to IR analysis and bond strength determination.

2.2.1.2 Flame Treatment

The apparatus used was the laboratory flaming rig at Plastics Division, ICI Ltd, Welwyn. It consisted of a rotating spindle with a spigot, to which a bottle could be attached and a burner, which could be brought close to the bottle, (see photo 1). The distance between burner nozzles and bottle was 50mm. The burner was 150mm wide with 94 holes. The flame was a natural gas/air mixture, the flow of which could be adjusted. A polyethylene film was attached to a bottle by means of double sided tape and then the flaming was carried out. The polyethylene film was then reversed and treated on the other side. The films were handled only by their edges. After treatment, the edges in contact with the tape were cut off. The films were stored in the dark until needed.

2.2.1.3 Corona Discharge.

The apparatus used was the corona discharge equipment at Plastics Division, ICI Ltd., Welwyn. The treating equipment was made by Lepel High Frequency Laboratories, and the haul off gear by Bone Brothers. A single electrode was used and the distance between the electrode and film was 0.15mm in all cases. Polyethylene film was taped onto a roll of film already in the machine, and then treated. The film was then removed and turned round and the procedure repeated. Thus films treated on both sides were obtained. Various speeds and control settings were used. Identical procedures were employed for polypropylene films.

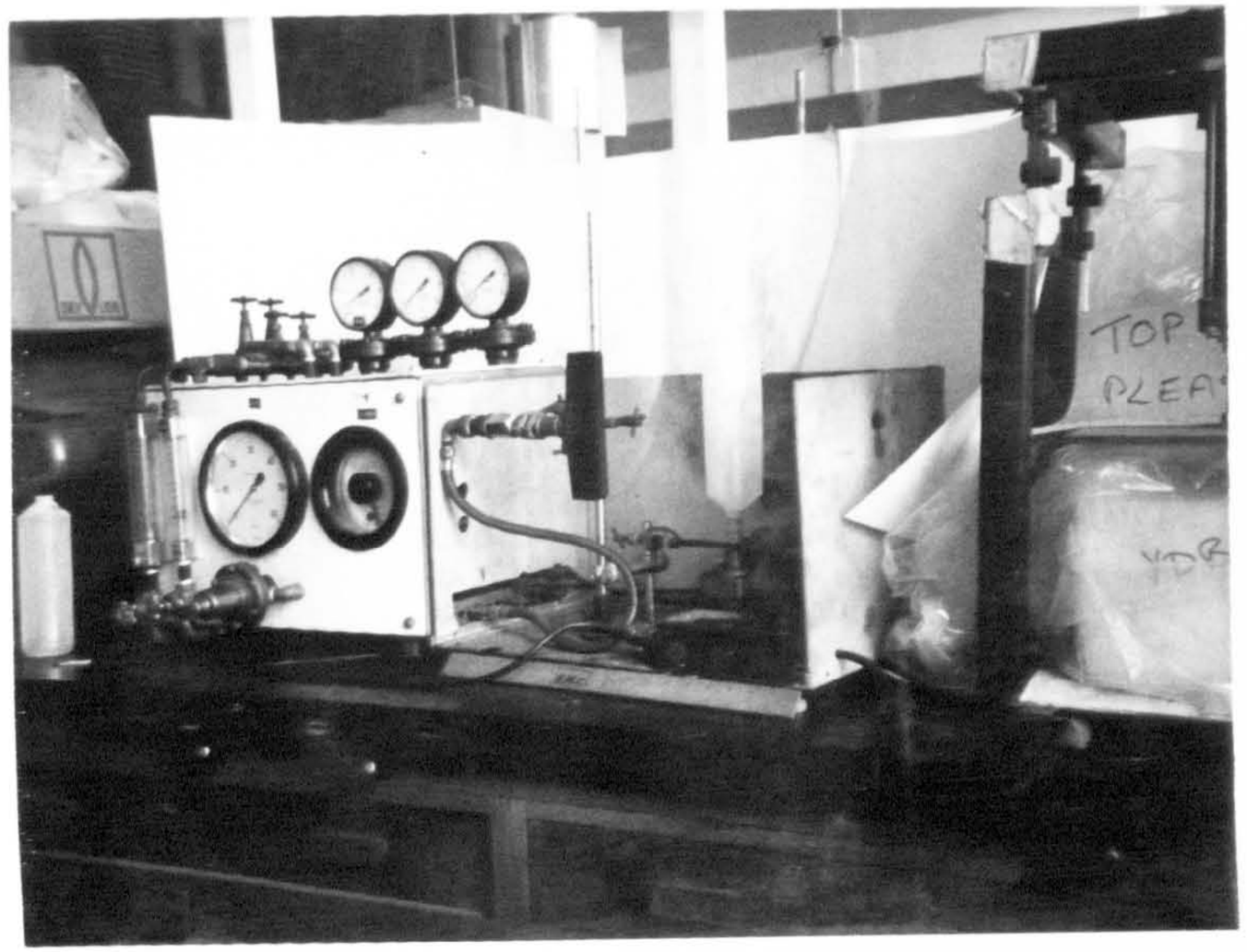


Photo 1.

Bottle rig at I.C.I. Plastics Division.

2.2.1.4 Nucleation, in Contact with Aluminium.

Aluminium foil was degresed, using trichloroethylene in a soxhlet extractor, dried in a hot air oven and then etched in a chromic acid bath for 7 minutes at 65°C. (Chromic acid composition:- $Na_2Cr_2O_7.2H_2O$: H_2O : H_2SO_4 = 1:30 : 10 parts by weight). The foil was then washed with agitation in twelve changes of distilled water. Polyolefin films were then compression moulded between two sheets of foil for the conditions specified later in a laboratory press. The laminates formed were then cooled rapidly by passing water through the plattens of the press. "Blanks" of the polyolefin films were prepared by compression moulding between sheets of poly(ethylene terephthalate). The aluminium was removed by dissolution in 2M sodium hydroxide solution. To avoid possible overheating, the reaction was kept at below 5°C, and stirred vigorously. Residual traces of metal contaminants were removed by concentrated hydrochloric acid at 5°C. The films were washed with distilled water and dried under vacuum. In one experiment, the aluminium foil was removed by peeling, and both exposed polymer surface and the foil inner surface examined by XPS.

2.2.1.5 Extrusion Coating of Aluminium with Polyethylene.

The apparatus used for extrusion coating is shown in Fig.11 and is the property of ICI Ltd., Plastics Division at Welwyn. The extruder is made by Modern Plastics Machinery Corporation (UK) Ltd., and has a 90mm diameter barrel with an LD ratio of 25:1. The line has a single turret unwind and a two roll wind up with manual changeover. The ozone shower unit is made by Softal GmbH of Hamburg.

The aluminium foil was passed through on a paper backing to prevent tearing. Polyethylene ("Alkathene" WNC71) was extruded first with a nozzle temperature of 200°C and then 300°C. The line speed was set

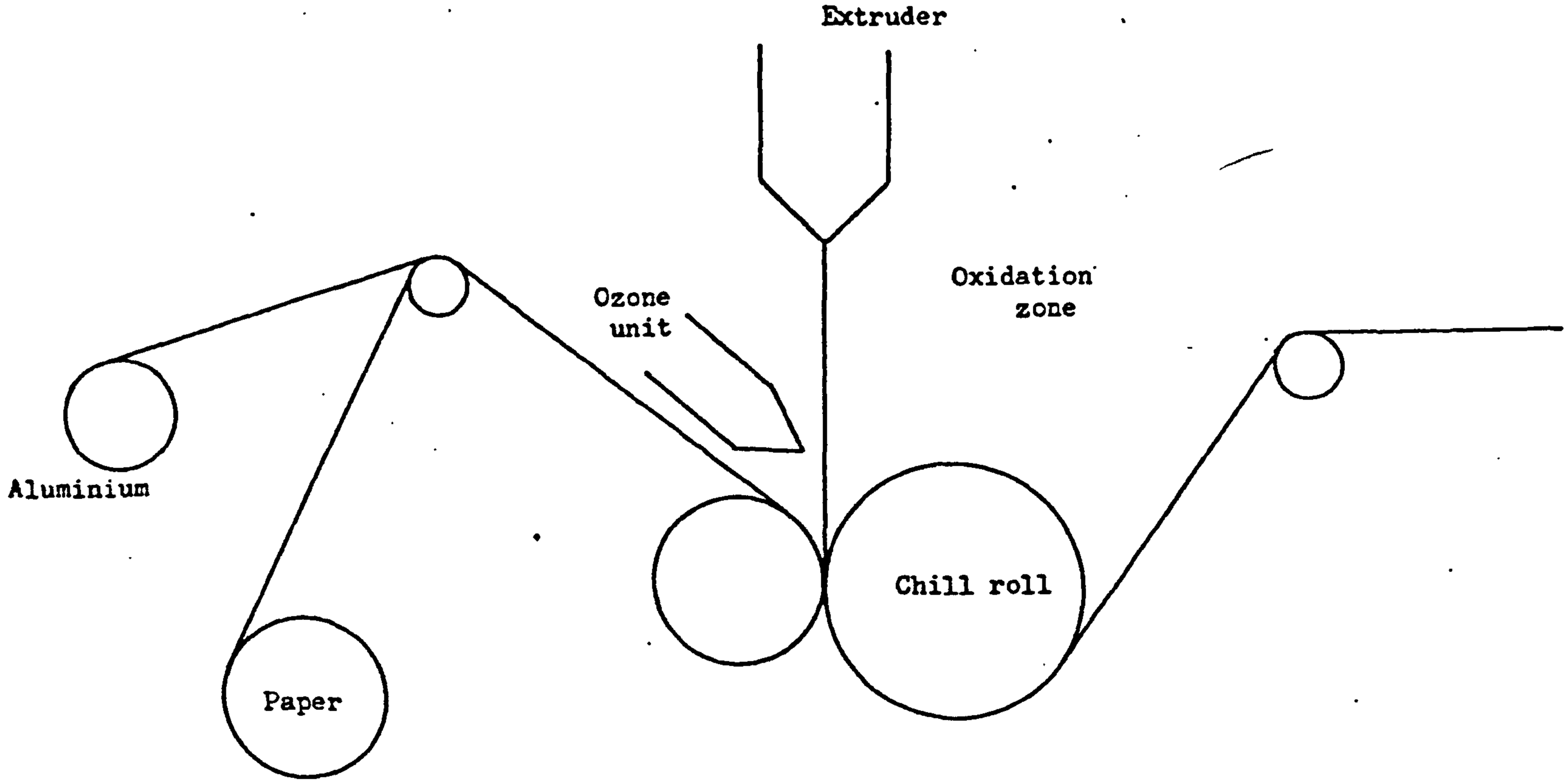


Fig.11. Schematic representation of the extrusion coating unit.

at 254mm per second to give a polymer coating thickness of 0.125mm. In some cases, the polyethylene was given an "ozone shower" first, prior to coating, applied by directing a stream of ozonised air at the molten web just prior to its contact with the foil (see fig.11). Composite lap joints were made for bond strength determinations in a manner similar to that described later. The lap joints consisted of aluminium strip-epoxide adhesive-laminate-epoxide adhesive-aluminium strip; the laminate consisted of polyethylene film extruded onto aluminium.

Before bonding, both the aluminium foil and polyethylene sides of the laminate were treated with chromic acid ($K_2Cr_2O_7$: H_2O : H_2SO_4 = 7:12:150 parts of weight). The acid was applied by means of a glass fibre brush. A Border of 10mm was left untouched to prevent any contact with the polymer-metal interface. After 60 seconds, the acid was washed off with distilled water and the laminate dried under vacuum.

A small sample of each different treatment was taken for XPS studies. To avoid contamination due to handling, the samples were taken from the centre of the treated areas and handled with clean tweezers. Next, after marking the side not in contact with aluminium, the metal was removed by dissolution with 2M aqueous sodium hydroxide solution, under the conditions mentioned above (see 2.2.1.4). The samples were then dipped into concentrated hydrochloric acid, washed with distilled water and dried under vacuum. Before bonding, both the aluminium foil and polyethylene sides of the laminate were treated with chromic acid.

2.2.1.6 Effects of organic liquids and vapours on polyolefins.

"Alkathene" WJG47 and "Rigidex" 50 films were placed in soxhlet extractors. These were then fitted with condensers and attached to flasks containing either hexane or hexane-heptane (5:1) mixtures. After a suitable time, the films were removed and subjected to vacuum, usually for 120 minutes. In the initial stages, a mechanical pump was used to obtain vacua, later "Zeolite" sorption pumps were employed. The latter gave values of 10^{-3} torr. Bonding took place on removal from vacuum. Films used for ageing tests were kept in the dark in previously cleaned glass containers.

"Alkathene" WJG47 and "Propathene" HF20 films were also subjected to trichloroethylene at 50°C, as well as to its vapour. After treatment, such samples were subjected to vacuum as above.

2.2.1.7 Other Methods of Treatment.

A 0.26M solution of ammonium persulphate in distilled water was prepared. Polyethylene films were immersed in this at 70°C for sixty minutes, then washed with distilled water and dried under vacuum.

A 5% solution of benzoyl peroxide in methylene dichloride was prepared. "Alkathene" WJG47 films were dipped into this for five minutes and then placed in an air oven at 90°C for twelve hours.

"Alkathene" WJG47 films were placed in a clean reaction flask and placed in a circulating air oven at 90°C for varying times.

2.2.1.8 Extraction of Treated "Alkathene" WJG47.

Glass tubes with No.2 sintered glass discs were cleaned with hot chromic acid, rinsed well with distilled water and dried. They were then extracted with trichloroethylene for 24 hours and dried to constant weight. The polymer film to be extracted was placed in the

tube and weighed. The tube was then placed in a soxhlet extractor. The sample was then extracted with trichloroethylene or xylene for a given time. The tube and film were then dried to constant weight. It was found necessary to have the top of the sintered tube at least 15 mm above the top of the syphon tube, to prevent any losses of undissolved film.

The method was applied to "Alkathene" WJG47 treated with chromic acid and ammonium persulphate solution. In both cases an untreated film was also extracted.

The residue obtained from the polyethylene treated with chromic acid, was treated with hot 50:50 aqueous ethanol, dimethyl formamide and then acetone. The weight losses are recorded in the results section.

2.2.1.9 Use of Polyethylene as the Adhesive.

1. Initial experiments.

Suitably treated aluminium strips (127 x 25.4 x 3mm) and bulldog clips were placed in a thermostatically controlled oven at required temperatures for 30 minutes. Then the strips were removed and placed together with a piece of polyethylene film between them, so that a 25.4mm overlap of the aluminium strips with polyethylene in between, was obtained. A bulldog dip was used to hold the assembly together. The joint was then quickly replaced in the oven for the specified length of time. On removal from the oven the joint was allowed to cool at room temperature for one hour before being used for bond strength determinations.

2. Final Experiments.

To overcome the various difficulties experienced in the initial experiments, a suitable jig (see fig.12) capable of holding 5 samples, was made from aluminium. This ensured that a 25.4mm overlap between aluminium strips could be achieved every time. Before each experiment,

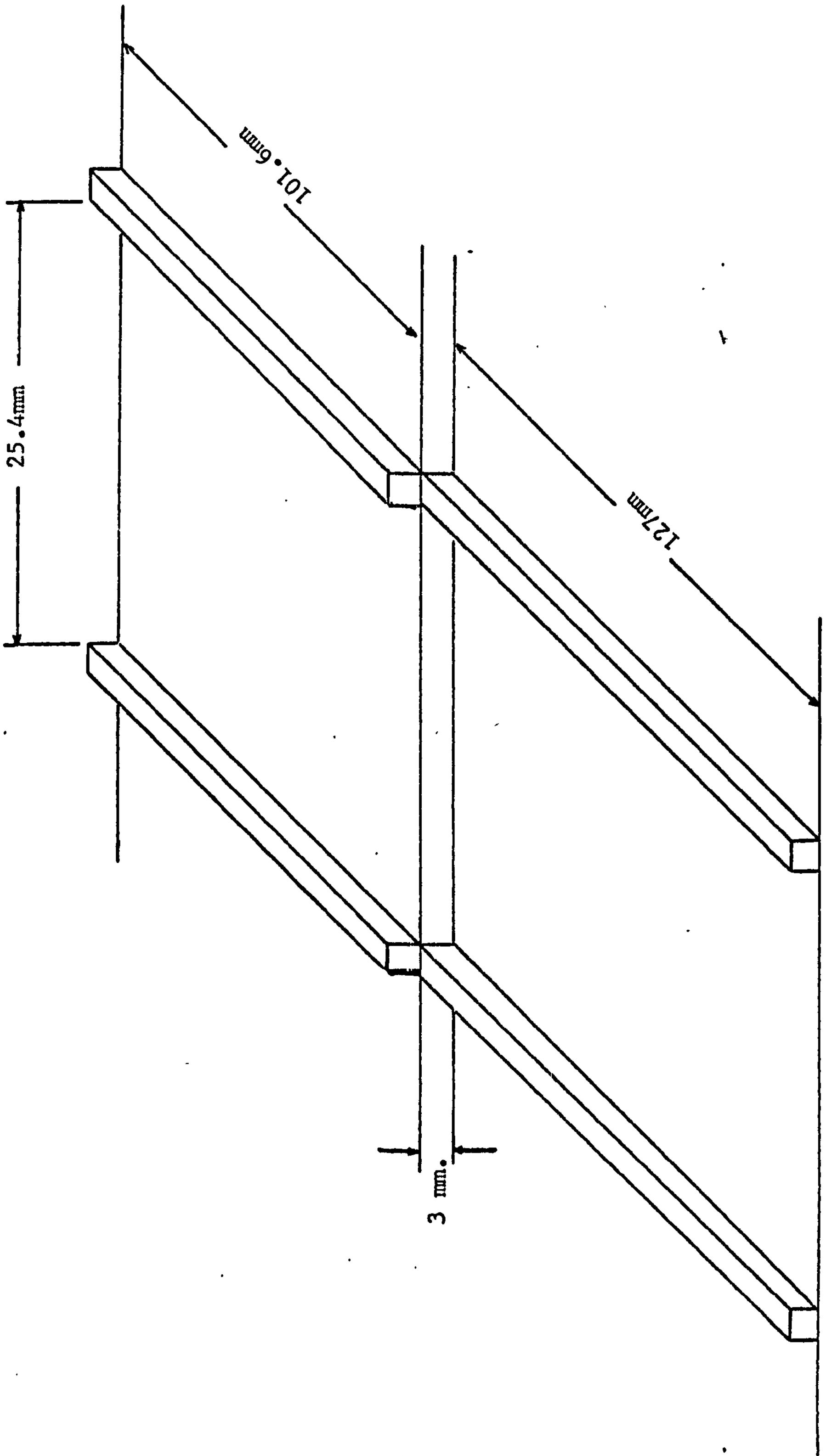


Fig.12.

Diagramatic representation of jig used in experiments with polyethylene as the adhesive.

the whole jig was liberally sprayed with a mould release agent in a fume cupboard fitted with a strong fan. This was to prevent contamination of any other material. To ensure constant thickness of the polyethylene layer, three spacers made from 0.076mm diameter wire were placed on the 25.4mm overlap space of each lower aluminium strip. The upper aluminium strip was placed in position and the assembly, including weight, was placed in the oven at the required temperature for 30 min. The upper bars were then quickly removed, dipped onto "Alkathene" WJG47 so that a 25.4mm square at one end was covered with molten polyethylene. This was rapidly replaced in the jig, so that it gave polyethylene in contact with the spacers on the lower aluminium bar. The weight was then placed to hold the joints in place and the assembly left in the oven for the required time. On subsequent removal from the oven, the samples were allowed to cool for one hour before being used in bond strength determinations.

It is possibly spurious to note that the operation of melting polyethylene onto the upper strips and replacing these in position, was carried out as quickly as possible to prevent heat loss.

2.2.2 Pretreatments for Polytetrafluoroethylene.

1. Apparatus Used.

A conventional two-compartment cell was used (see fig.13). This was cleaned with hot chromic acid, well rinsed with distilled water and dried before use. The two compartments were separated by a sintered glass disc. This was covered by a thin gel on the anode side. The gel was prepared by dissolving ethyl cellulose in electrolyte solution. The electrolyte was a solution tetrabutyl-ammonium tetrafluoroborate (0.1 mol dm^{-3}) in dimethyl formamide. The anode was a platinum wire electrode, and an aqueous saturated calomel electrode was used as the reference

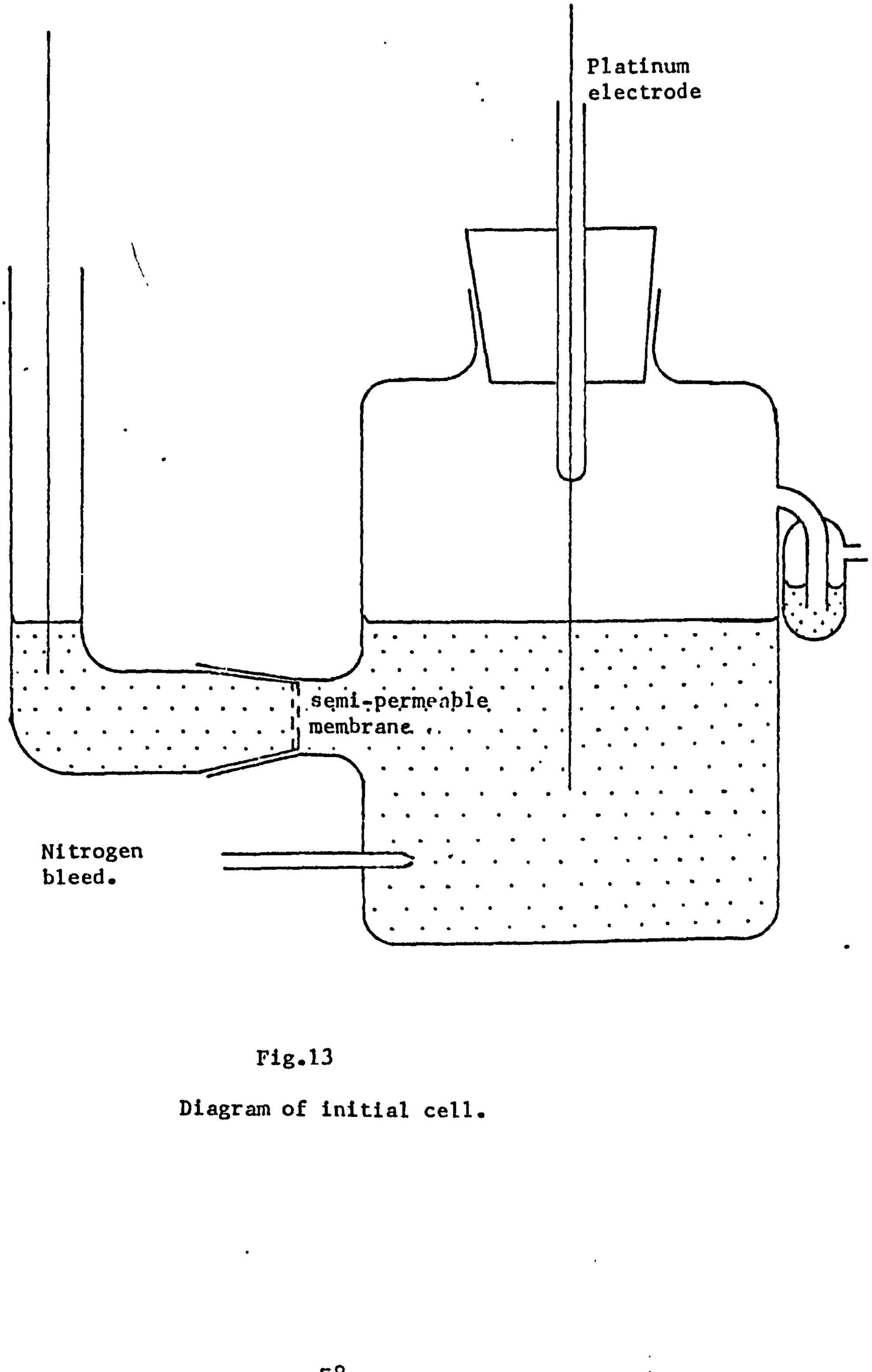


Fig.13

Diagram of initial cell.

electrode. Thus all voltages quoted are against the saturated calomel electrode.

All the experiments were carried out under nitrogen. Reducible impurities were removed before each experiment by pre-electrolysis at -2.5 volts for 30 minutes. All the experiments were carried out potentiostatically, using a Chemical Electronics TR70/2A potentiostat. Later, the cell was modified by having the anode closer to the cathode, in an attempt to reduce the cell resistance.

2. Preparation of Electrolyte.

The support electrolyte, tetrabutylammonium tetrafluoroborate, was prepared by the method described by House (94).

Tetrabutylammonium hydroxide (25 millimoles) was dissolved in the minimum volume of distilled water. This solution was then neutralized with fluoroboric acid (26 millimoles), in an ice bath. The resulting mixture was stirred at room temperature for one minute, and the solid filtered and washed with distilled water, till the washings were neutral. The crude product was recrystallized three times from an ethyl acetate-pentane mixture. On drying, a white crystalline solid with a melting point of 153-155^{o}C was obtained.

Dimethyl formamide was purified by the method described by Brummer (95). Commercial DMF was dried for 48 hours over activated molecular sieves. It was then purified by distilling at reduced pressure (2mm of mercury), the first 10% of the distillate being discarded. The solvent was stored over molecular sieves.

3. Reduction by Contact with an Electrode.

A film of polytetrafluoroethylene was held in close contact with the cathode which had been prepared from a lead-antimony grid. A potential of -2.5 volts was applied for five minutes. The film was then moved

and the procedure repeated till the whole film had been treated.

In a similar manner, a polytetrafluoroethylene film was held in close contact with a platinum wire cathode. Various voltages were applied and the cell current and the effect on the film were noted.

4. Reduction by Means of Radical Anions.

1. Using the Initial Cell.

With the initial cell (see fig.13) varying amounts of naphthalene were added to the support electrolyte, and electrolysis was carried out at -2.45 volts. The electrolysis were carried out for varying times. The effect of concentrated nitric acid on treated polytetrafluoroethylene films, was studied.

Other compounds likely to produce radical anions were used in place of naphthalene and their effects on polytetrafluoroethylene were observed.

2. Using the Modified Cell.

With the modified cell, (see fig.14) a concentration of naphthalene in electrolyte of 0.55% W/V was used. The polytetrafluoroethylene films were subjected to electrolysis for varying times. The cell current was noted every 15 minutes. Eventually, the lead electrode was replaced by a platinum one.

The effect of fuming nitric acid at different conditions was studied on the treated films. The loss in weight after treatment with fuming nitric acid, was found. After washing with DMF and acetone, the treated films were vacuum dried and weighed. After treatment with fuming nitric acid, the films were washed in 12 changes of distilled water and vacuum dried to constant weight.

The effect of electrolysis on polytetrafluoroethylene, filled with bronze, was also studied.

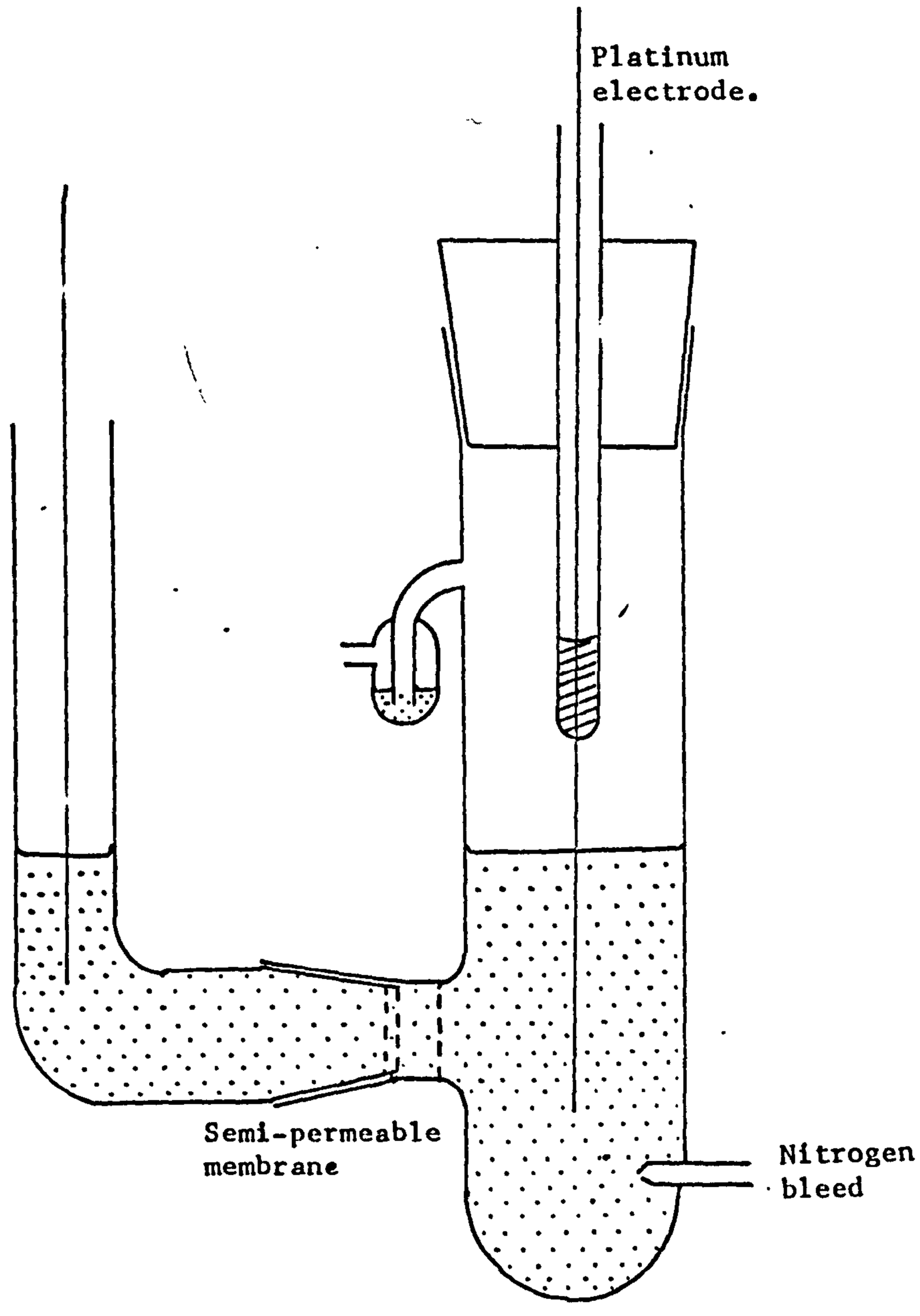


Fig.14

Diagram of modified cell.

2.2.2.5 Reduction by Means of Sodium Naphthalide.

This is a well known conventional treatment for polytetrafluoroethylene and was carried out for comparison purposes.

A sodium-naphthalide 1:1 mole ratio complex, was prepared by dissolving sodium metal (5.75gm) and naphthalene (32gm) in previously dried tetrahydrofuran (250 mls).

Polytetrafluoroethylene films were then dipped into this complex for varying lengths of time. The samples were then removed, washed with clean dry tetrahydrofuran and then with acetone. Subsequently, the films were dried under vacuum.

2.3 Comparison of bond strengths of polyethylene and ethylene-vinyl acetate copolymers.

In this set of experiments the bond strengths of untreated "Alkathene" WJG47 and the two ethylene-vinyl acetate copolymers, A14271 and 24-03 were determined. Lap shear joints were made and tested as described in section 2.4.

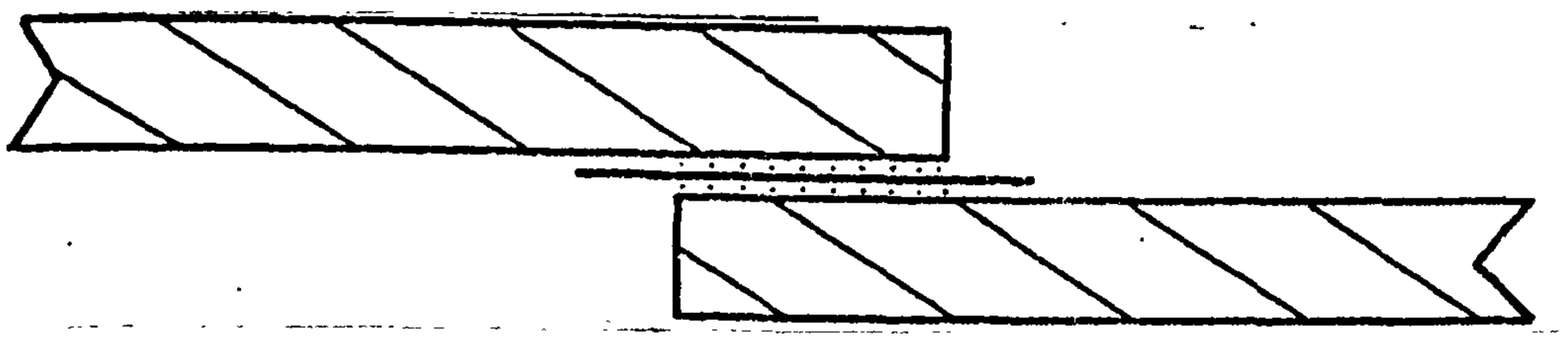
The modulus values for "Alkathene" WJG47 and ethylene-vinyl acetate 24-03 were determined using an Instron. As there is no relevant British Standard method, values for 1% modulus were obtained using a withdrawal rate of 5mm s^{-1}.

2.4 Preparation and Testing of Adhesive Joints.

Aluminium strips were cut from bars and their edges were milled square, to give them required dimensions (127 x 25.4 x 3mm). The strips were then degreased with trichloroethylene in a soxhlet extractor, then rubbed down with emery paper (grade 400) and treated with chromic acid for 10 minutes at 70°C. The chromic acid composition was potassium dichromate, one part by weight; distilled water, ten parts by weight; and concentrated sulphuric acid, thirty parts by weight. The strips

were thoroughly washed with distilled water and dried in a circulating air oven for five hours at 70°C.

Single lap shear joints were made, using the "Araldite" AV/100-HV/100 adhesive system. Spacers made from wire of 0.076mm diameter were used to ensure a constant thickness. It was later found that this thickness could be reproducibly achieved without the use of spacers. The laminate was made so that a 25.4mm square of polymer film was covered. The polymer film sample was slightly larger (37 x 37mm), to prevent the adhesive adhering to the opposite aluminium strip. The joints were



held in position by means of bulldog clips, giving a pressure of 3000 Kg m^{-2}, and cured in an air oven at 60°C for three hours. The joints were then removed and allowed to cool down for one hour at room temperature.

Bond strengths were determined, using a Hounsfield Tensometer (W type) at a withdrawal rate of 0.104mm per second. The results quoted, unless otherwise stated, are the mean of at least ten determinations. Throughout the bonding operations, the films were handled only with clean tweezers and even then, only at the edges. For other operations required, clean new gloves were used.

2.5 Attenuated Total Reflectance Spectroscopy (ATR).

Attenuated total reflectance spectra were carried out, using a KRS-5 crystal with a 9 fold reflectance, fitted to a Beckman Aculab spectrophotometer. The polyolefin films were backed with filter paper, which

permitted a better degree of contact between the film and the KRS-5 crystal.

In a few cases, spectra were made using a Wilks MIIR 9T attachment with a KRS-5 crystal capable of 25 fold reflectance, fitted to a Perkin Elmer 457 spectrophotometer. This equipment was the property of Plastics Division, ICI Ltd., Welwyn.

2.6 Contact Angle Measurements.

Where practicable, contact angles were measured immediately after treatment. Drops of distilled water were placed on the film surface by means of a microsyringe.

Initially, contact angles were measured by projecting the image of the drop onto a screen and measuring the angle of that. Photographic means of recording the contact angle were also tried, but unsuccessfully.

In the end, contact angles were measured, using a goniometer eyepiece with cross wires fitted to a cathetometer. Results quoted are the mean of at least six determinations and have an accuracy of $\pm 2^{o}$. Measurements were carried out within 30 seconds of placing the drop. The drop volume was 50 microlitres and was delivered by means of a microsyringe.

2.7 X-Ray Photoelectron Spectroscopy (XPS)

The determinations were carried out on an AEI ES 200B electron spectrophotometer equipped with a Mg Kα source (exciting energy 1253.6eV) rated at 500 watts, but normally run at 300 watts. Binding energies were corrected to C1s = 285.0eV for the untreated polyolefins. The instrument was calibrated so that the Au 4f $^{7}/2$ peak had a binding energy = 840eV relative to the Fermi level. Binding energies were considered accurate to $\pm$ 0.2eV.

Samples were examined in the form of rectangles (approx. 20 x 6mm) and mounted on the probe tip with a double sided adhesive tape. The working pressure inside the spectrophotometer chamber was 10^{-8} torr.

2.8 Talysurf Measurements.

Samples of polyethylene film of various treatments were stuck onto glass slides by means of double sided tape. These samples were then vacuum plated with aluminium for 1 minute.

The samples were then placed in the Rank Taylor Hobson Talysurf and their roughness recorded onto heat sensitive paper. Several traces from different parts of each sample were made to ensure that these were reproducible.

3. Results

3.1 Results of Polyolefin Pretreatments

3.1.1 Chromic Acid Etching.

The XPS data vs bond strength results for polyethylene and polypropylene are shown in Tables 1 and 2. It can be seen from Table 1 that sulphur and oxygen are increasingly incorporated into the polyethylene surface as etching progresses. In the case of polypropylene, however, Table 2 shows the extent of modification to be the same, irrespective of treatment time. Thus polypropylene etched for 1 min at 20°C the values are similar to those of polypropylene etched for 6 h. at 70°C.

XPS spectra (spectrum 1) show the effect of etching on the polyethylene films. It can be seen that the pure polyolefin films reveal very clean surfaces. There is some evidence of oxidation, but the oxygen peaks are very small. It is worth noting that only samples etched for 6 h. at 70°C showed any evidence of chromium and then only in trace quantities. The intense sulphur peak is relatively sharp and thus considered to be indicative of a single species, - SO_3H. The oxidised carbon species were found to be C-OH, C=O, and -COOH.

XPS spectra 2 and 3 show the valence band spectra of polypropylene and polyethylene before and after chromic acid etching. Incorporation of oxygen into the surfaces of the polymers is shown by growth of the band at c1222eV. As can be seen, there is little change in the polypropylene spectrum, while there is increase of band intensity at 1222eV in the polyethylene spectrum.

Table 3 provides O1s to O2s peak ratios for etched polyolefin films. The limiting O1s:O2s ratio for the instrument used was •9. It can be seen that with polypropylene mild treatments affect the polymer only to

a fraction of the sampling depth. This is in agreement with angular rotation experiments.

Table 4 shows the chemical changes in the surface of polyethylene caused by concentrated sulphuric and chromic acids as determined by ATR infra-red spectroscopy. It can be seen that at 20°C there is no evidence of chemical changes. Polypropylene shows no chemical changes even with prolonged etching at 70°C. In the case of polyethylene treated with concentrated sulphuric acid, new peaks appeared at c1200 and c1050cm^{-1}. These were assigned to the $-SO_3H$ group. After treatment with chromic acid at 70°C for four minutes, changes were observed in polyethylene spectra. New peaks at c3500, c1630, c1200 and c1050cm^{-1} appeared. (see fig.15). With increasing treatment, the broad peak at c1630cm^{-1} developed a shoulder at c1720cm^{-1}, which on further treatment became a new peak.

Treating the etched films with 2M sodium hydroxide, ethereal diazomethane and 2,4-dinitrophenyl hydrazine (see figs.16-18) showed that C=O and COOH groups were present. The presence of these groups agrees with XPS results.

When the chromic acid system was replaced by chromium trioxide in acetic acid, peaks at c1710 and c1630cm^{-1} were obtained. Increase in treatment time or a fourfold increase in chromium trioxide concentration caused the c1710cm^{-1} peak to increase and the c1630cm^{-1} peak to decrease (see fig.19). Treatment with 2,4-dinitrophenyl hydrazine (see fig.20) and 2M sodium hydroxide (see fig.21) showed that the peak at c1710 to be due to C=O and -COOH groups.

"Reduction" of polyethylene film treated with chromium trioxide/acetic acid mixture showed that with sufficiently long treatment times, modifications of the surface occurred. The final spectrum (see fig.22)

shows an untreated surface. The colour of the film changed from a light brown to the clear of an untreated film. The bond strength, however, was 6.62MNm^{-2} and the contact angle 73^{o}.

Contact angle determinations show a general decrease with treatment time for polyethylene. In the case of polypropylene, after an initial decrease, contact angles increase with time of treatment. An increase in contact angle for polyethylene is obtained after etching for 6 h. at 70^{o}C when the acid is not changed.

SEM Micrographs of severely treated polypropylene surfaces show an increase in surface roughness, (micrograph 2). Talysurf traces of severely treated polyethylene surfaces also show considerable roughening (see fig.23c). However, mild treatments (fig. 23b) appear to show no increase in surface roughness at all.

Severely treated polyethylene and polypropylene films (6 hours at 70^{o}C) were extracted with trichloroethylene and xylene for 24 hours. Only in the case of polyethylene etched with chromic acid was an insoluble residue obtained. This was 1% by weight of treated film and in the form of brown needles. Attempts were made to dissolve this with various solvents (Table 5), but without much success. Table 6 shows the effect of reducing the potassium dichromate concentration in the chromic acid composition. As can be seen, there is evidence of oxidation. Comparison with a severe concentrated sulphuric acid treatment, shows that higher oxidation and adhesion levels are obtained with the former.

Ageing appears to have little effect on the bond strength of chromic acid treated film. Table 7 and graph 1 show that after over one year's ageing, there is only a slight decrease in bond strength.

3.1.2 Results of Flame Treatment.

Two types of polymer were used, additive free "Alkathene" WJG47 and "Alkathene" WJG11, the same polymer but containing 0.02% antioxidant. For each film the gas to air ratio was approximately the same, about 4.2 to 1. For normal settings, the flow rates were 37 and 150cm^3 sec^{-1} for gas and air respectively. In each case the film spent 1.2 seconds in the flame. Some samples were also treated for four times this period.

XPS results and bond strength data are shown in Table 8. Untreated films showed very low levels of oxidation when examined by XPS. Typical spectra from polyethylene surfaces before and after flame treatment are shown in spectrum 4. It can be seen that oxidation of the treated surfaces took place. Nitrogen functions were also found to be included in the surface. The following groups were identified: C-OH; C-O-C; COOH; and C=O as well as NH_2. The existence of these groups could not be confirmed by ATR, as spectra of film treated for ten times the normal period did not show any difference from untreated.

The valence band spectra of flame treated samples (spectrum 5) are very similar to those for polyethylene etched with chromic acid (spectrum 3). Again there is growth of the peak at 1222eV.

Long term ageing of treated films (Tables 9-11 and graphs 2-4) did not show a large decrease in adhesion, nor was there much difference in XPS spectra of aged films.

Talysurf work (fig.24) and SEM (micrograph 3) examination did not show any changes in surface topography.

3.1.3 Results of Corona Discharge Treatment.

Polypropylene, additive free and 0.02% antioxidant containing polyethylene were examined. Various levels of treatment were used. The

XPS and joint strength data are shown in Tables 12 and 13. As can be seen, treatment causes chemical modification of the surface. The usual oxygen containing species of nitrogen functions in the form of NH_2 and NO_2 were found in the surface after treatment.

None of the treatment levels showed any changes in surface chemistry, when examined by ATR. The polypropylene samples were found to have become very brittle after treatment. No changes of surface topography were noted with SEM or talysurf (fig.25) examination.

Long term ageing of treated samples did not appear to have a drastic effect on the bond strengths. (Tables 14, 15 and graphs 5 and 6).

3.1.4 Results of Nucleation in Contact with Aluminium.

XPS spectra of untreated polyethylene reveal very little oxygen in the surface (spectrum 6a) - less than 0.25 atomic %. There was no evidence of polyethylene being transferred to poly(ethylene terephthalate). Melting against aluminium produced an increase in oxygen levels (spectrum 6b). Joint strengths and oxidation levels for polyethylenes melted against different substrates are summarised in Table 16. The main group identified was C=O, but increases in unsaturation were also noted. No evidence of sodium or aluminium which could possibly be present in the surfaces was found. Small N1s peaks were observed in some of the treated samples. In the case of "Rigidex" 50 melted at 175°C strong SiO_2 peaks were observed and since these interfere with O1s peaks, no O:C values are available. Control experiments established that sodium hydroxide - hydrochloric acid treatment, did not affect the surface chemistry or bond strength of the polyethylene.

In a different experiment a "sandwich" of "Rigidex" 50 melted between aluminium foil at 150°C was prepared. One foil was peeled off and both the resulting surfaces were analysed by XPS. The polyethylene surface

gave an O:C ratio of 0.92%, while the aluminium foil surface revealed the characteristic oxide on metal spectrum together with an intense C1s peak. Spectrum 7 contrasts the C1s and Al2p spectra from this surface, and from aluminium foil degreased and acid etched prior to the melting experiment.

XPS results show a higher level of oxidation for high density polyethylene. Bromination results in Table 17 show some interesting difference. These show that there appears to be a significant increase in unsaturation, especially in the case of low density polyethylene, after melting against aluminium.

ATR and transmission infra-red spectra did not show any chemical changes in the surface of treated films. Contact angles showed a decrease, more in the case of low density than high density polyethylene.

SEM micrographs (micrograph 4) show a flat surface with little mounds. These are thought to be imprints of the etched aluminium surface.

3.1.5 Results of Extrusion Coating.

A different low density polyethylene, "Alkathene" WNC71 was used for these experiments. Additive free and polymer with two antioxidant loadings, 0.2 and 0.02% was examined. The XPS data for these films, as well as joint strengths are recorded in Table 18. A small untreated sample of each polymer was obtained by pressing against poly(ethylene terephthalate) film for 5 minutes at 150°C. XPS examination shows that treatment increases oxygen and nitrogen content of the surface (see spectrum 8). A plot of nitrogen and oxygen to carbon ratios against adhesion levels is shown in fig.26. This gives a correlation of 0.94 for the oxygen line and 0.82 for the nitrogen line. From XPS determination the groups introduced were -C-OH and -C=O for oxygen, and $-NH_2$ for nitrogen.

ATR spectra of the most severe conditions, extrusion at 300°C with ozone shower did not show any changes in surface chemistry.

3.1.6 Effect of Organic Liquids and Vapours on Polyolefins.

Tables 19 and 20 show the effect of hexane and hexane-heptane mixtures on "Alkathene" WJG47 and "Rigidex" 50. It can be seen that there is a moderate increase in bond strength. Too long exposures to the solvents cause environmental stress cracking. Table 21 shows the effect of ageing on hexane extracted "Alkathene" WJG47. The first result was carried out without a control. Subsequent determinations used controls. The control consisted of bonding a few samples after extraction, and ensuring that there was an increase in bond strength. Talysurf profiles (fig.27) show a certain amount of surface roughness. Table 22 shows the effect of trichloroethylene at 40°C on polyethylene and trichloroethylene vapour on polypropylene. Swelling of polyethylene by about 25% occurred on immersion in trichloroethylene.

3.1.7 Ammonium Persulphate and Peroxide Treatment.

The bond strength of polyethylene treated with 0.26M aqueous ammonium persulphate is shown in table 23. Extraction of the treated polymer gave 0.06% by weight insoluble residues. ATR spectra showed no change in surface chemistry.

Results of peroxide treated samples are also shown in table 23. Extraction of these samples gave no detectable insoluble residues. Untreated samples kept in the oven for the same time as peroxide treated samples show a decrease in bond strength.

3.1.8 Use of Polyethylene as the Adhesive.

Tables 24 and 25 and graph 7 show the effect of increasing temperature and "dwell" time on the effectiveness of polyethylene as an adhesive. With temperatures above 250°C, the polyethylene became yellow and brittle.

In the case of "dwell"time studies, it was noted that the wire spacers appeared to prevent the flow of molten polyethylene. Large voids could be seen near the spacers on bond rupture. The voids decreased with longer dwell times.

3.1.9 Comparison of Bond Strengths of Polyethylene and Ethylene-Vinyl Acetate Copolymers.

Table 26 shows the bond strength and modulus values for "Alkathene" WJG47 and two ethylene-vinyl acetate copolymers of different vinyl acetate content. Modulus values for ethylene-vinyl acetate 24-03 were not obtained, since there was not enough polymer available for testing.

3.2 Results of PTFE Pretreatments.

Table 27 shows the effect of potential on PTFE in contact with a platinum electrode. It can be seen that below 2.25 volts (w.r.t. standard calomel electrode) there was no apparent attack, but above this voltage blackening of the surface at point of contact occurred. Similar results were obtained using a lead electrode. It was noticed that this had a tendency to break down at the blackening voltage. Table 28 shows the values of bond strengths obtained for PTFE by direct contact and radical anion attack. Table 29 shows the effect of other radical anions on PTFE.

The radical anion attack gives a gradual darkening of surface until a shiny black film is obtained. This black layer slowly disappears with time (see micrograph 5) and is readily removed by concentrated nitric acid, leaving a yellow to off-white surface.

XPS results showed that the radical anion attack removed fluorine atoms from the PTFE surface. A carbon layer containing oxygen groups and some deposited lead was left. The effect of further treatment was

obscured by a thick layer of deposited lead. Treatment with nitric acid appeared to restore the original lead free PTFE surface with some oxygen containing species.

Because of problems associated with the lead electrode, it was replaced by a platinum one. The cell was also modified to reduce the high internal cell resistance. Table 30 shows the importance of cell current and possibly position in cell on bond strength. Table 31 shows the effect of hot fuming nitric on bond strength of blackened PTFE. A comparison with Table 30 shows a considerable loss of strength. For sample c in table 31, the thickness of the treated layer was calculated to be 150nm. (The density of the black layer, assumed to be carbon was assumed as 1). The effect of radical anion attack on the adhesion of bronze filled PTFE is shown by table 32. The joint strength of untreated samples is much higher for filled than unfilled PTFE. Radical anion attack does not increase the adhesion of bronze filled PTFE by a large amount.

Table 33 shows the effect of conventional pretreatment on the adhesion of PTFE. The adhesion results are comparable to severe radical anion attack.

With the exception of the commercial treatment, all other PTFE treatments were carried out under nitrogen. However, during one direct contact experiment, it was found that this treatment could be carried out in air. Using a platinum electrode it was then possible to work at higher voltages. It was noticed that with a voltage of 50v about 3 mm^2 of surface were blackened. The blackening was not uniform and appeared to follow the line of skiving marks, (see fig.28) irrespective of the position of the two electrodes to each other.

TABLE 1

XPS analytical data[a], contact angles and joint strength data for chromic acid etched polyethylene surfaces.

Etching Conditions	C:S atomic ratio	O:S atomic ratio	% O (not in SO_3 grps.) to total C	%C atoms with SO_3H grps.	Θadv deg.	Lap shear strength MN m^{-2}	Failure type [b]
Untreated	-	-	0.25	-	98	0.55	I
1 min/20°C Normal wash	269	14.9	4.40	0.37	76	7.45	M
30 min/70°C Normal wash	80.0	12.2	11.5	1.25	66	7.58	M
6 h /70°C Normal wash[c]	47.1	11.2	17.4	2.12	46	9.48	M
6 h /70°C Overnight wash[c]	59.2	14.1	18.6	1.69	64	6.96	M
6 h /70°C Normal wash[d]	74.2	11.0	10.1	1.35	105	6.74	M
6 H /70°C overnight wash[d]	73.8	11.9	12.1	1.36	85	7.83	M

Notes: a. All data refer to an electron emission angle (Θ) of 75°
b. I = Apparent interfacial failure. M = Failure of polyolefin film.
c. Acid changed every 2h.
d. Acid not changed.

TABLE 2

XPS analytical data[a], contact angles and joint strength data for chromic acid etched polypropylene surfaces

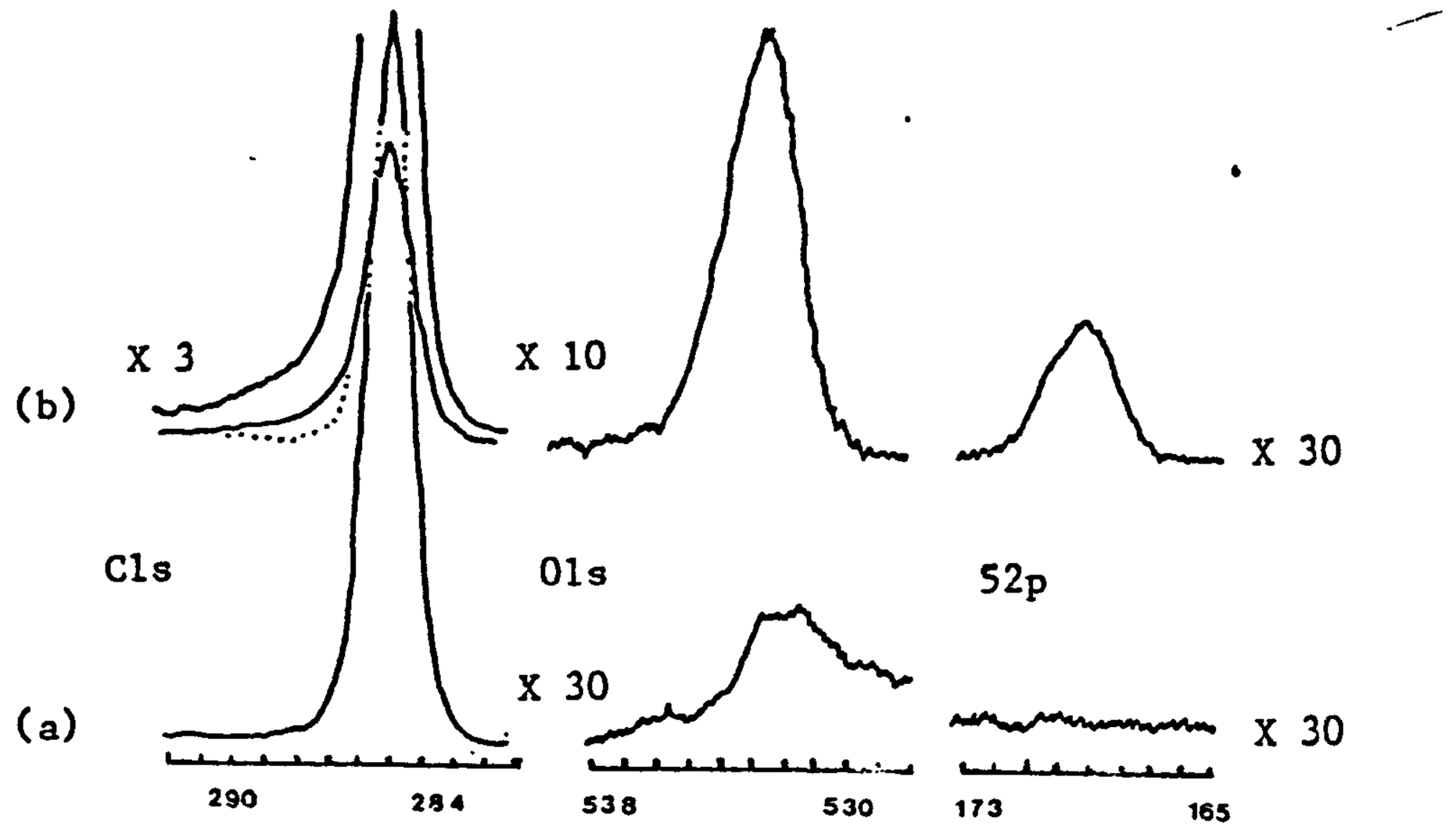
Etching conditions	C:S atomic ratio	O:S atomic ratio	% C atoms with SO_3H grps	%O (not in SO_3H grps) to total C	θ adv deg.	Lap shear strength MN m^{-2}	Failure type[b]
Untreated	-	-	-	0.25	92	0.28	I
1 min/20°C normal wash	283 (223)	19.1 (19.0)	0.35 (0.45)	5.9 (7.3)	73	4.69	I & M
1 min/20°C overnight wash	538 (307)	27.1 (19.4)	0.19 (0.33)	4.5 (5.3)	82	4.83	I & M
6 h/70°C normal wash	261	15.9	0.38	4.8	97	11.20	M
6 h/70°C overnight wash	380	14.0	0.26	4.3	94	11.65	M

a. Data refer to an electron emission angle (θ) of 75°, bracketed values to θ = 15°
b. I = apparent interfacial failure
   M = failure of polyolefin film

Spectrum 1.

Binding energies of core level peaks from polyethylene

(a) Untreated
(b) Chromic acid etched 30 min. at 70°C

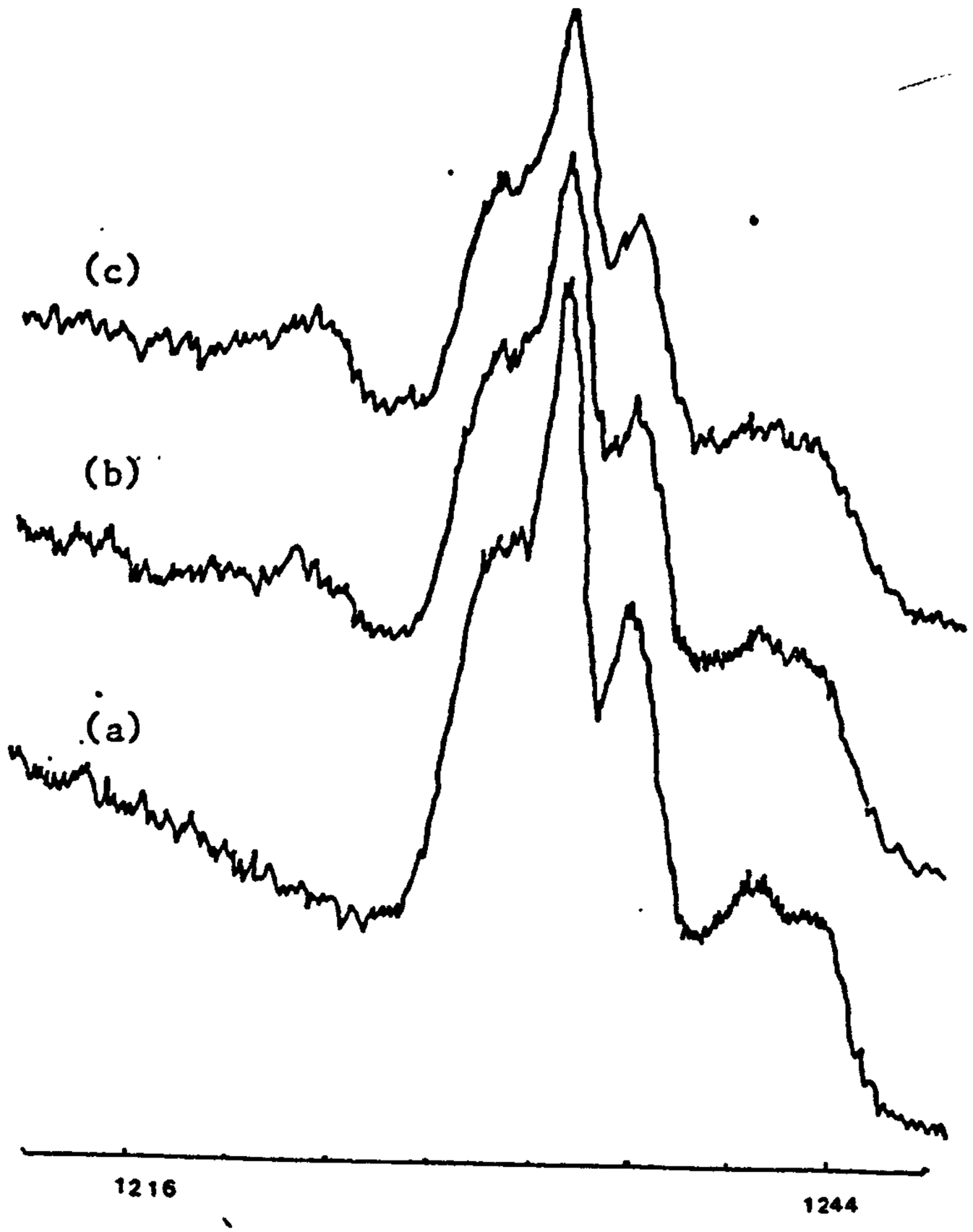


Binding energy eV

Spectrum 2.

Valance band spectra of polypropylene.

(a) Untreated
(b) Chromic acid etched 1 min. at 20°C.
(c) Chromic acid etched 6h at 70°C.



Kinetic Energy eV

Spectrum 3

Valance band spectra of polyethylene.

(a) Untreated
(b) Chromic acid etched for 1 min. at 20°C
(c) Chromic acid etched for 30 min. at 70°C

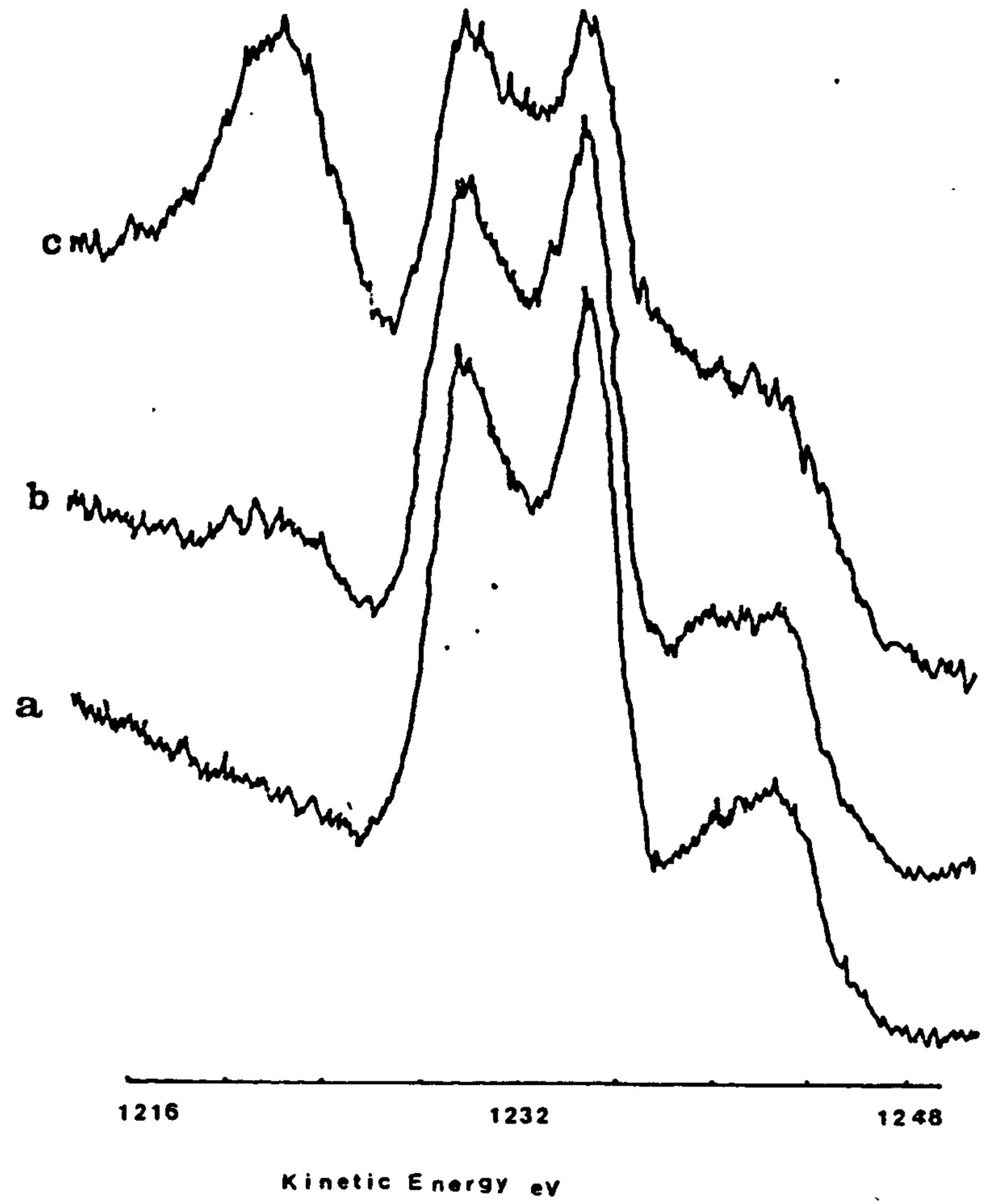


TABLE 3

O1s : O2s peak area ratio for etched films.

Polymer	Etching conditions (Normal Wash)	O1s : O2s[a]
PP	1 min/20°C	22.70
PP	6 h /70°C	13.70
PE	1 min/20°C	12.95
PE	30 min/70°C	9.15
PE	6 h /70°C	9.85

a Electron emission angle (Θ) of 75°

TABLE 4

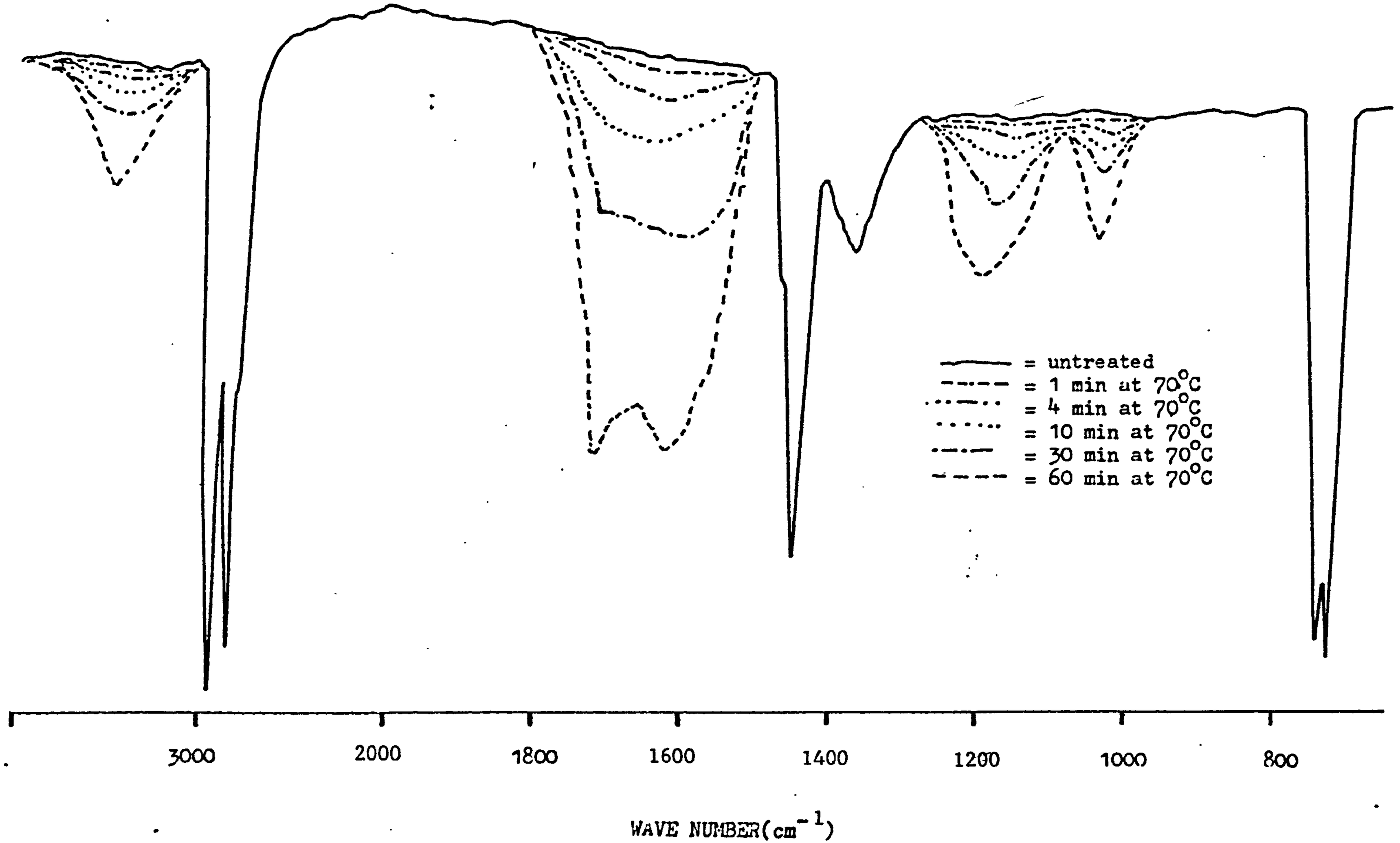
Treatment of "Alkathene" WJG47 with concentrated sulphuric and chromic acids

Reagent	Treatment Conditions	Lap Shear Strengths MNm^{-2}	ATR Results
None	-	0.55	Doublet c2900, doublet 720-730, single peaks c1460 and 1370cm^{-1}
Concentrated sulphuric acid	1 min at 20°C	0.97	No new peaks
Chromic Acid	1 min at 20°C	7.45	No new peaks
Concentrated sulphuric acid	60 min at 70°C	2.34	New peaks c1200 and 1050cm^{-1}
Chromic acid	60 min at 70°C	9.48	New peaks c3500, 1720 and c1630cm^{-1} peaks at c1200 and 1050cm^{-1} also present

Notes: Chromic acid composition = $K_2Cr_2O_7$: H_2O : H_2SO_4 = 7:12 : 150 parts by weight.

FIG.15

EFFECT OF CHROMIC ACID TREATMENT ON ATR SPECTRA OF "ALKATHENE" WJG47



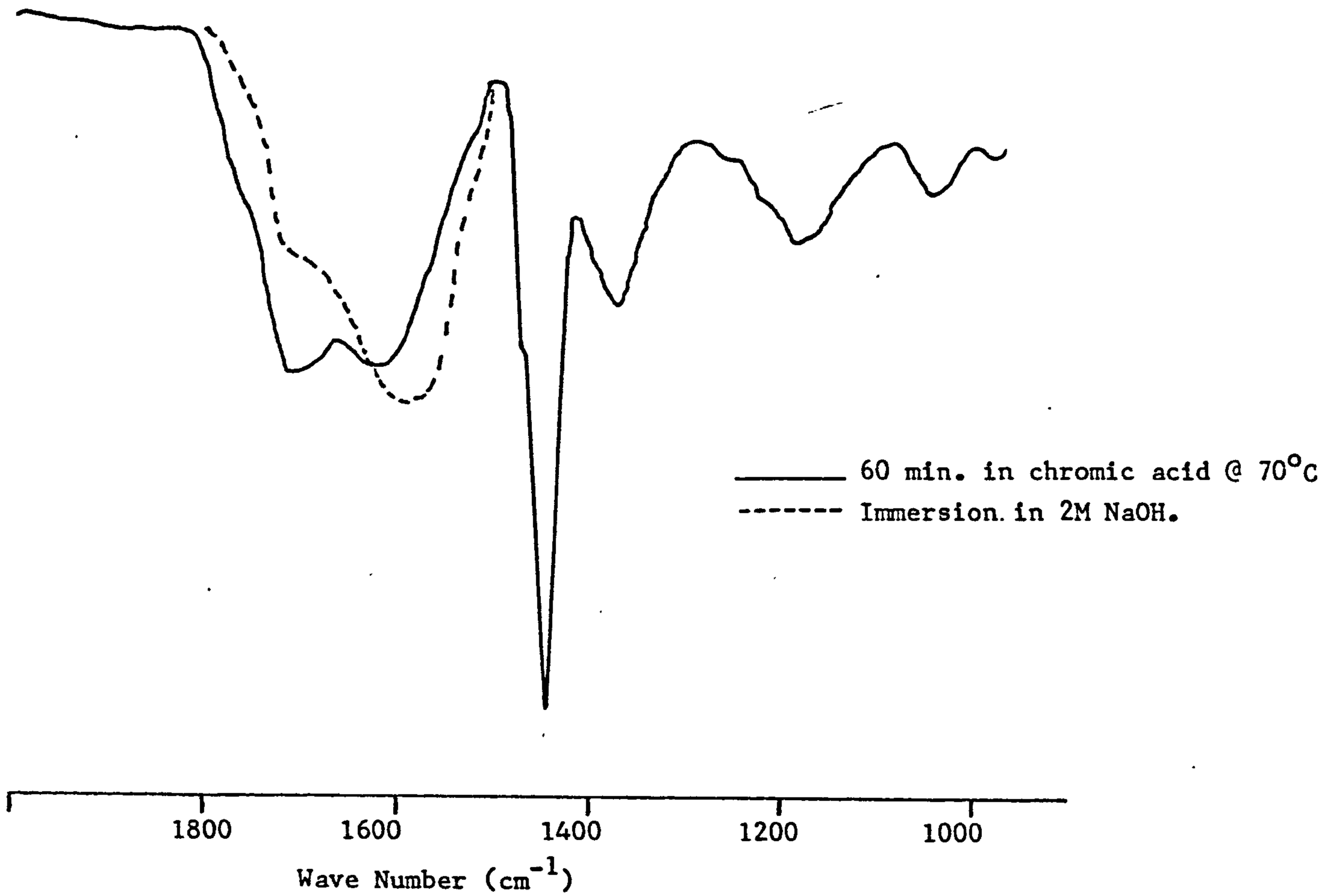


Fig.16
Effect of 2M Sodium Hydroxide Solution on Chromic Acid Treated Film

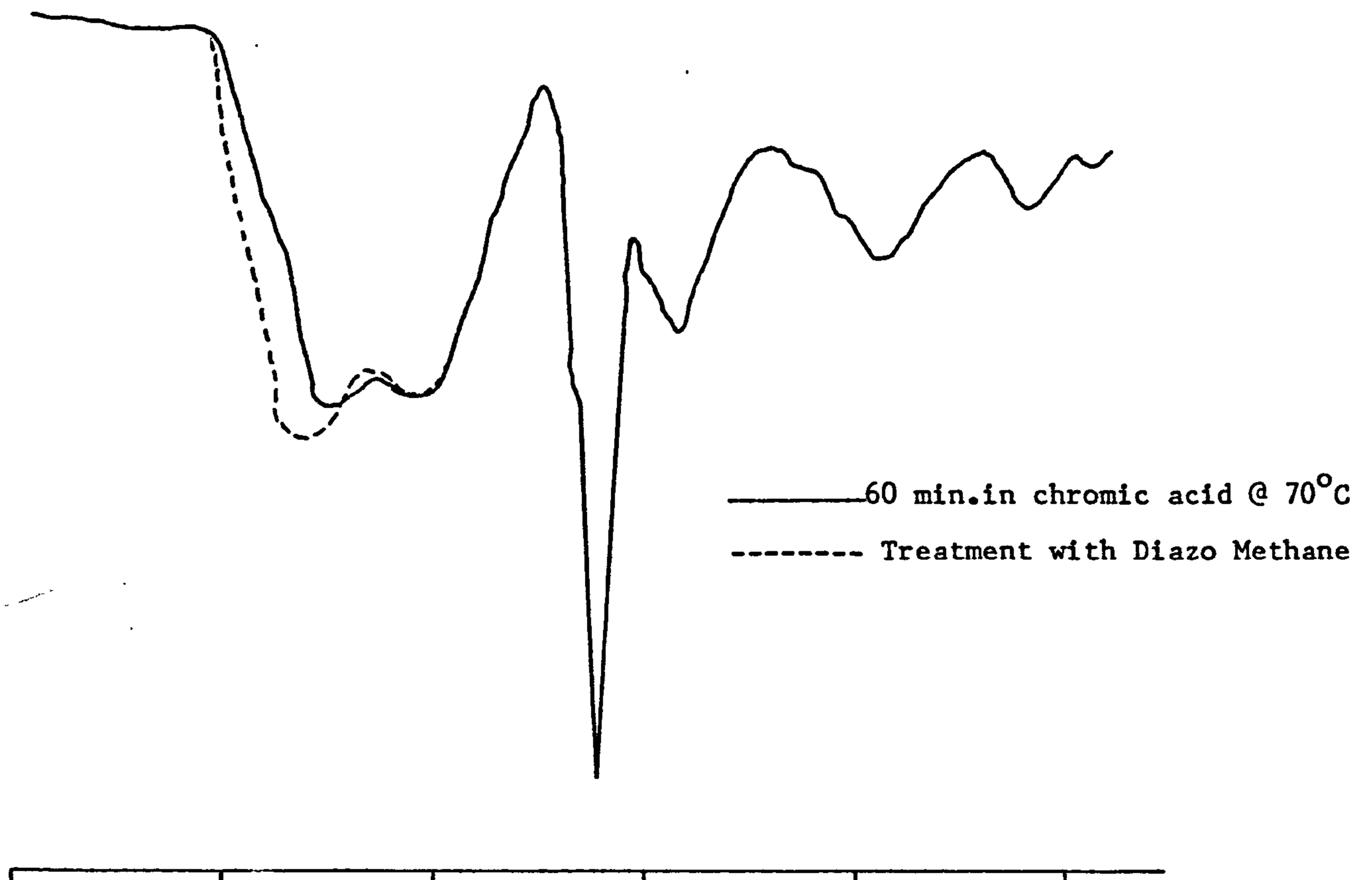


Fig.17
Effect of Diazomethane on Chromic Acid Treated Film.

Fig.18

Effect of 2,4-Dinitrophenyl hydrazine on chromic acid treated film

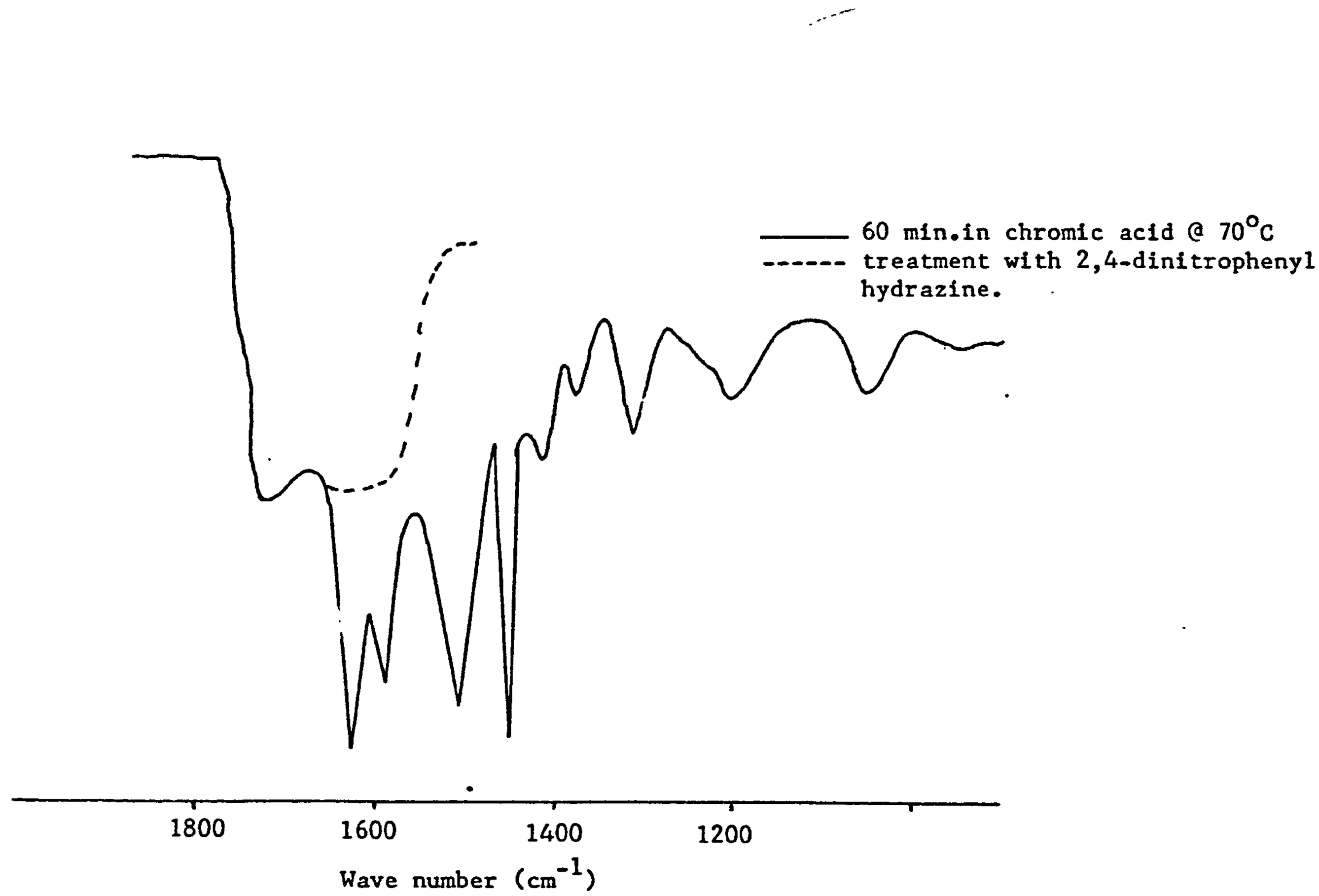


Fig.19

Effect of chromic acid ($CrO_3$1HAc) on polyethylene

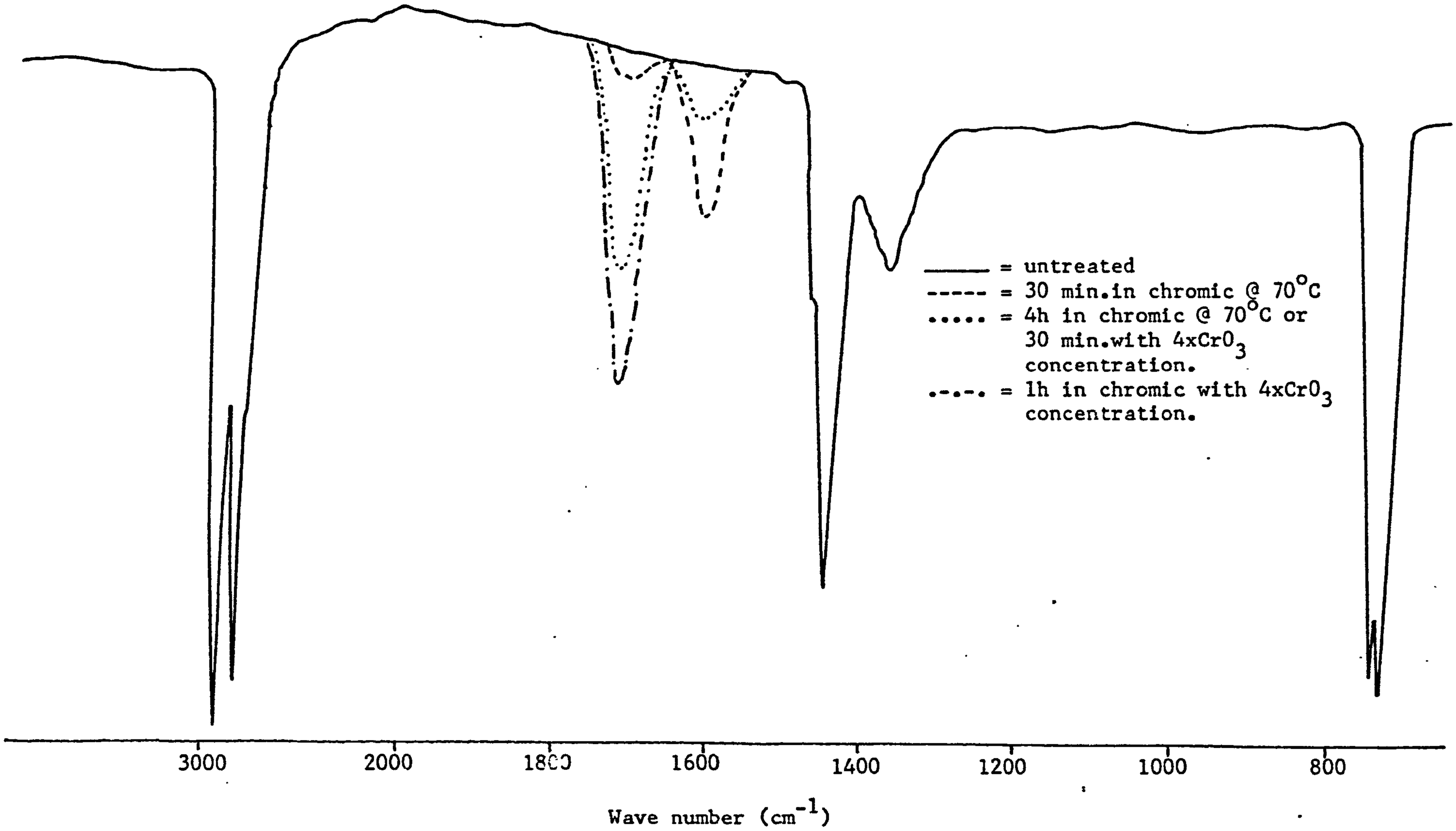


Fig.20

Effect of 2,4-dinitrophenyl hydrazine on polyethylene treated with chromium trioxide-acetic acid mixture.

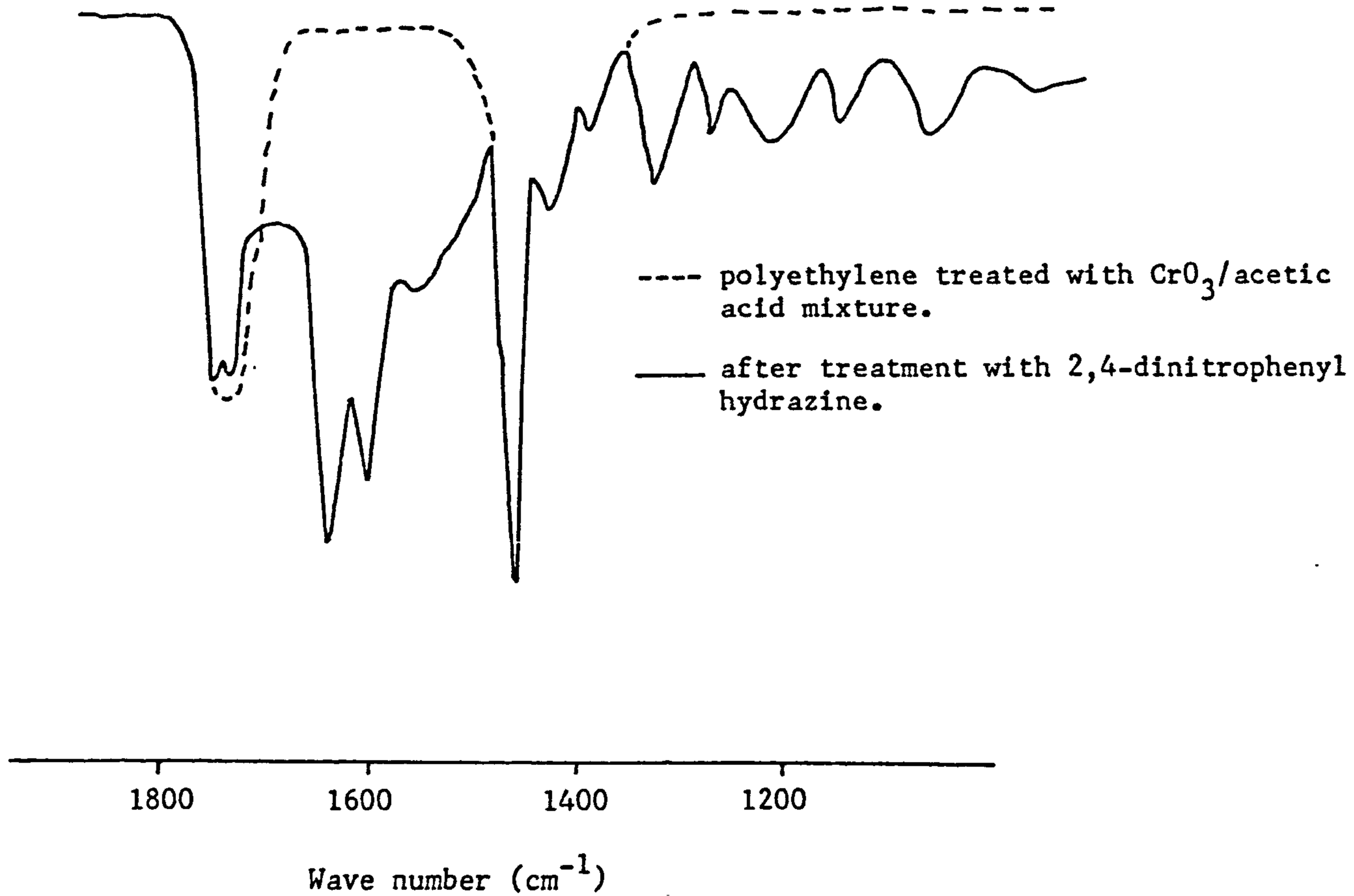
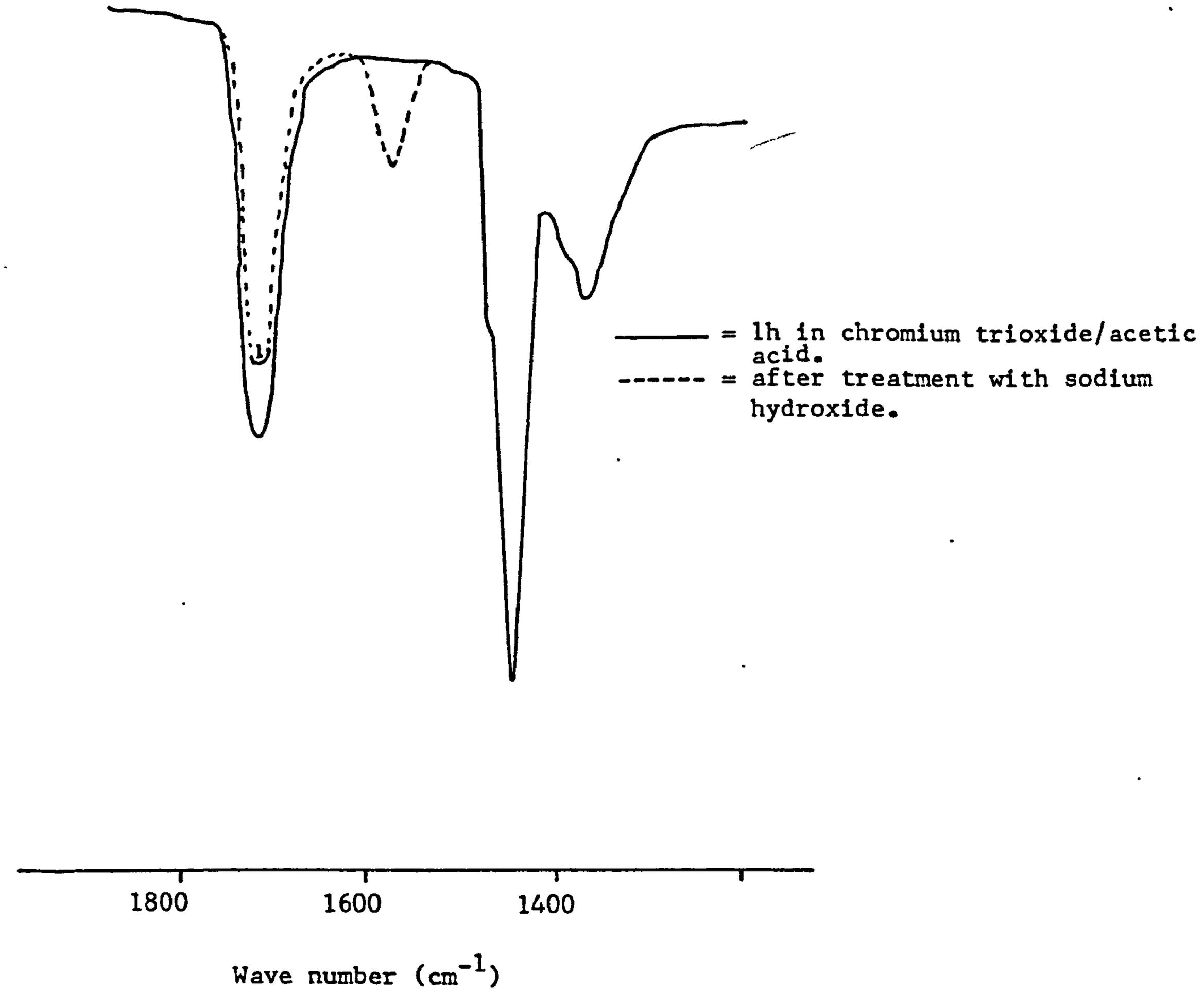
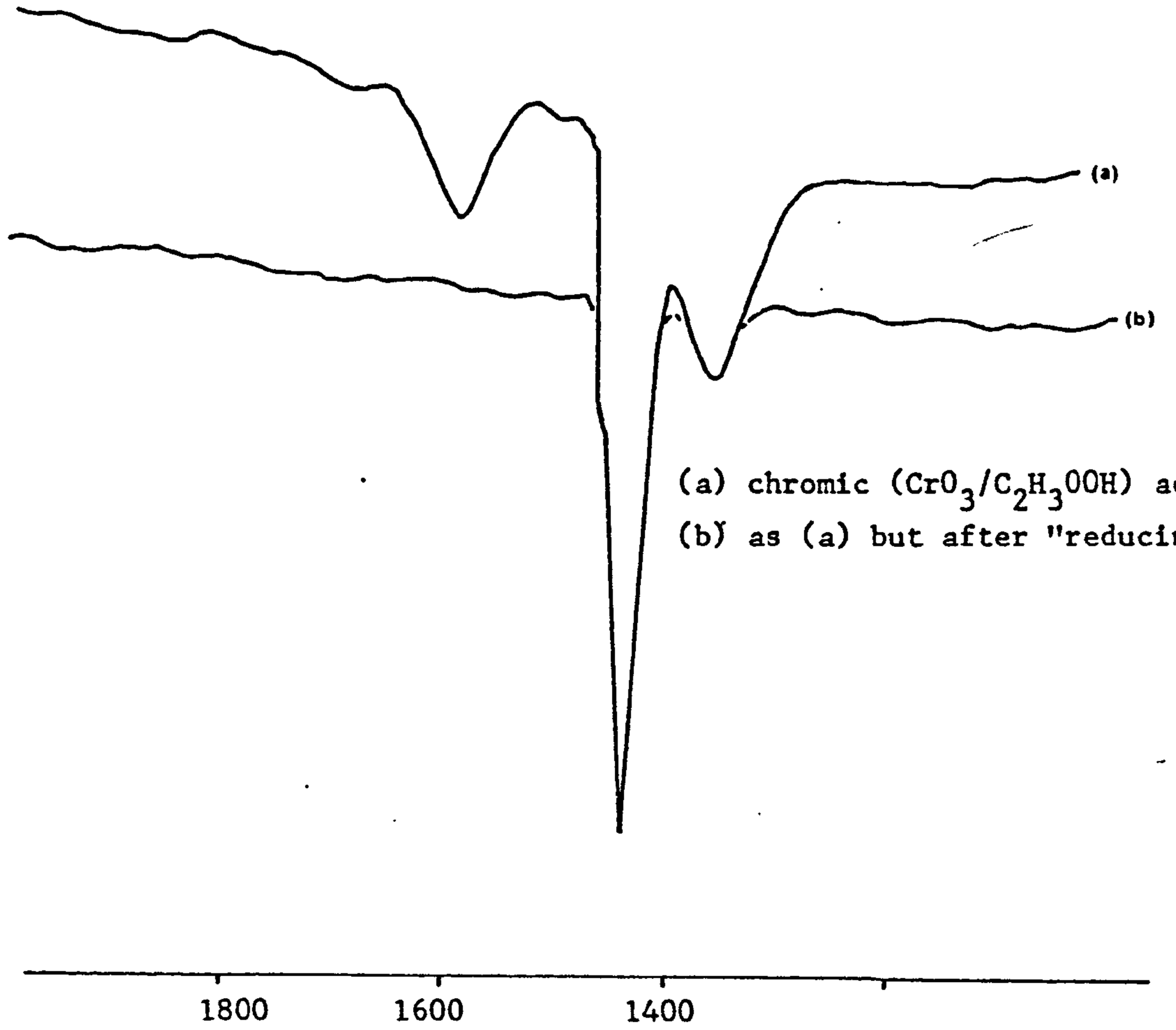


Fig.21

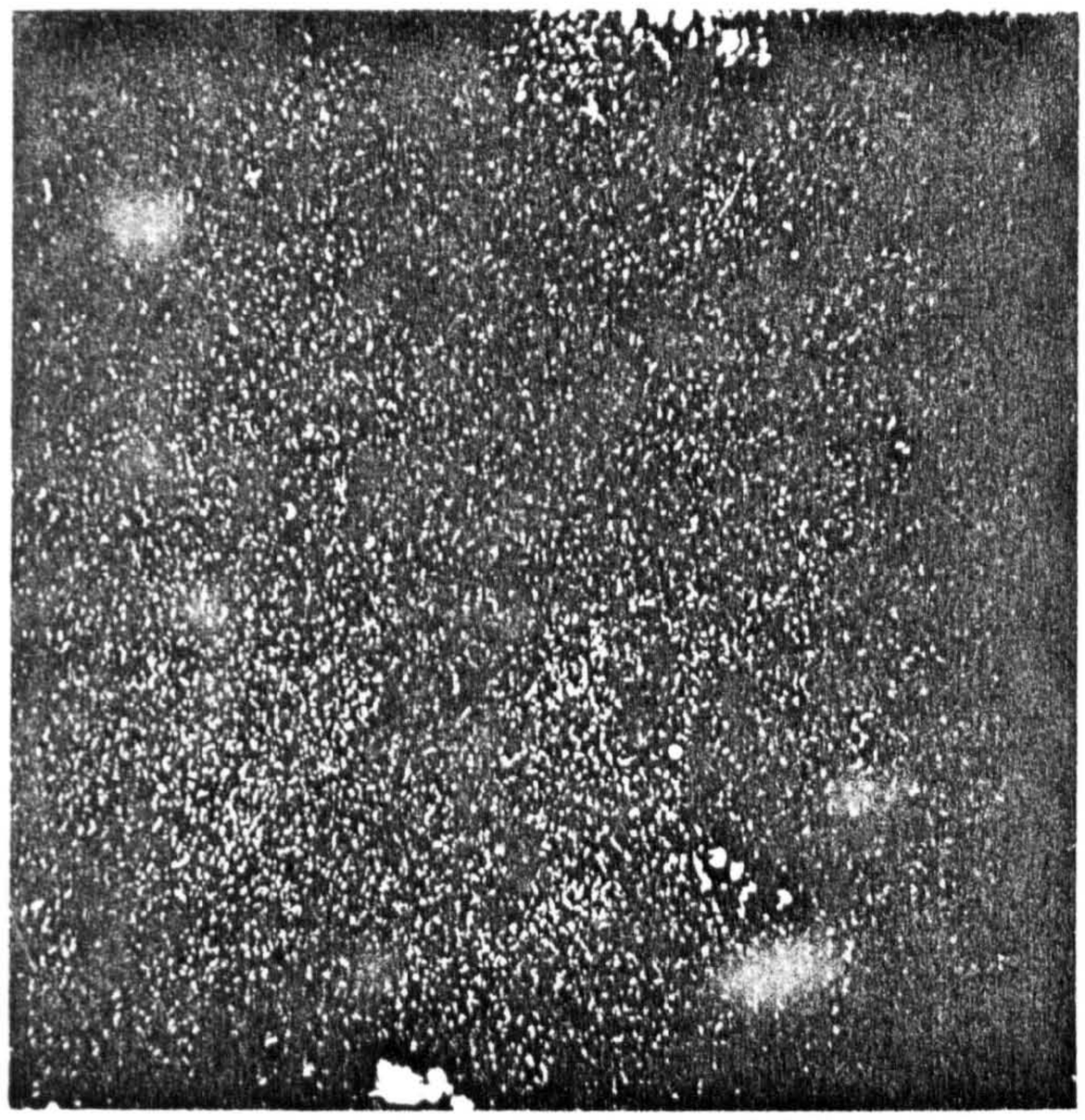
Effect of 2M sodium hydroxide on polyethylene treated with chromium trioxide/acetic acid.



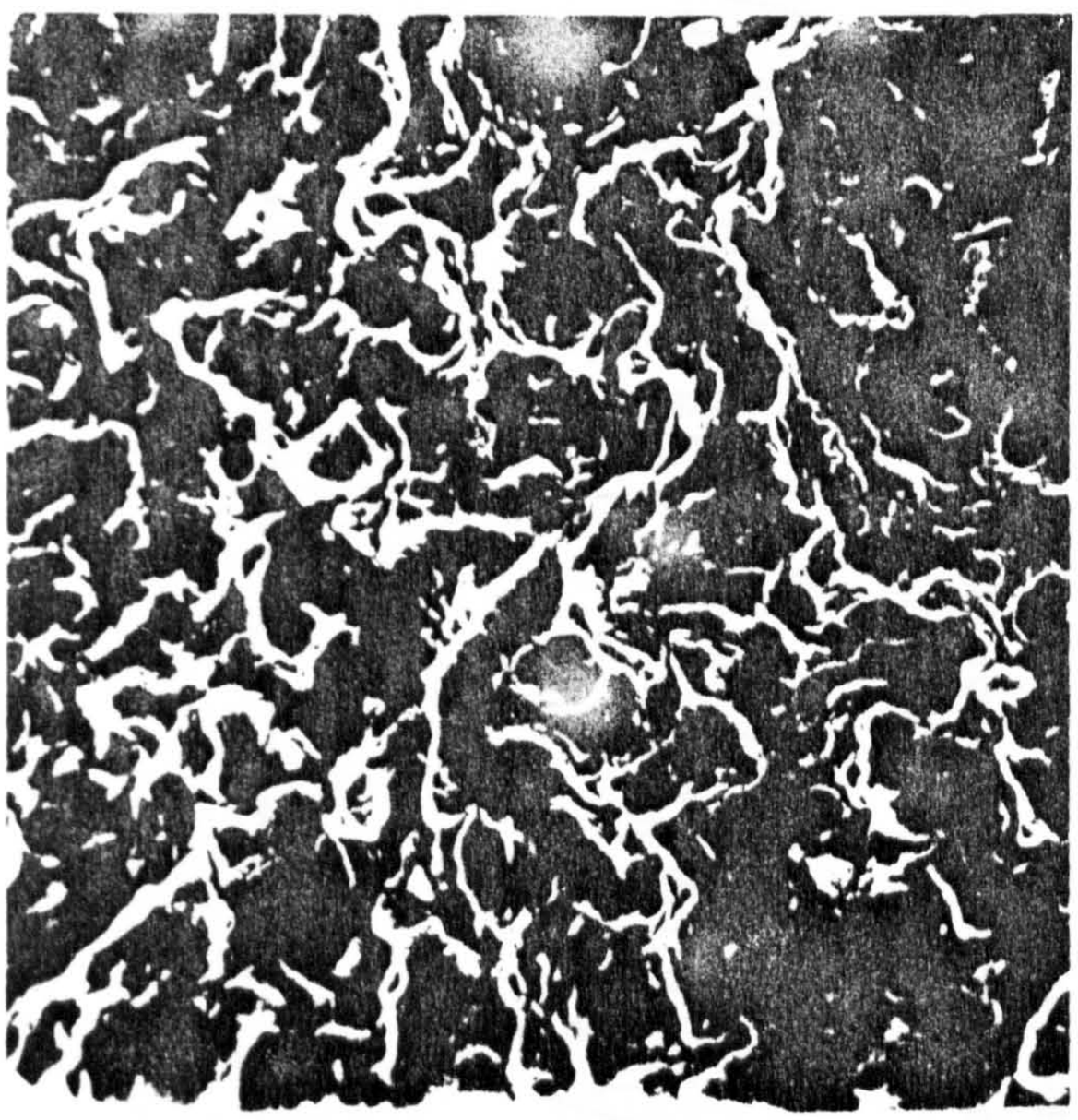


(a) chromic (CrO_3/C_2H_3OOH) acid treated
(b) as (a) but after "reducing" treatment.

Fig.22
ATR spectra of polyethylene before and after "reducing" treatment.



a.



b.

Photo-micrograph 2.

Effect of severe chromic acid treatment on polypropylene (mag. 2,100X)

(a) Untreated
(b) Treated

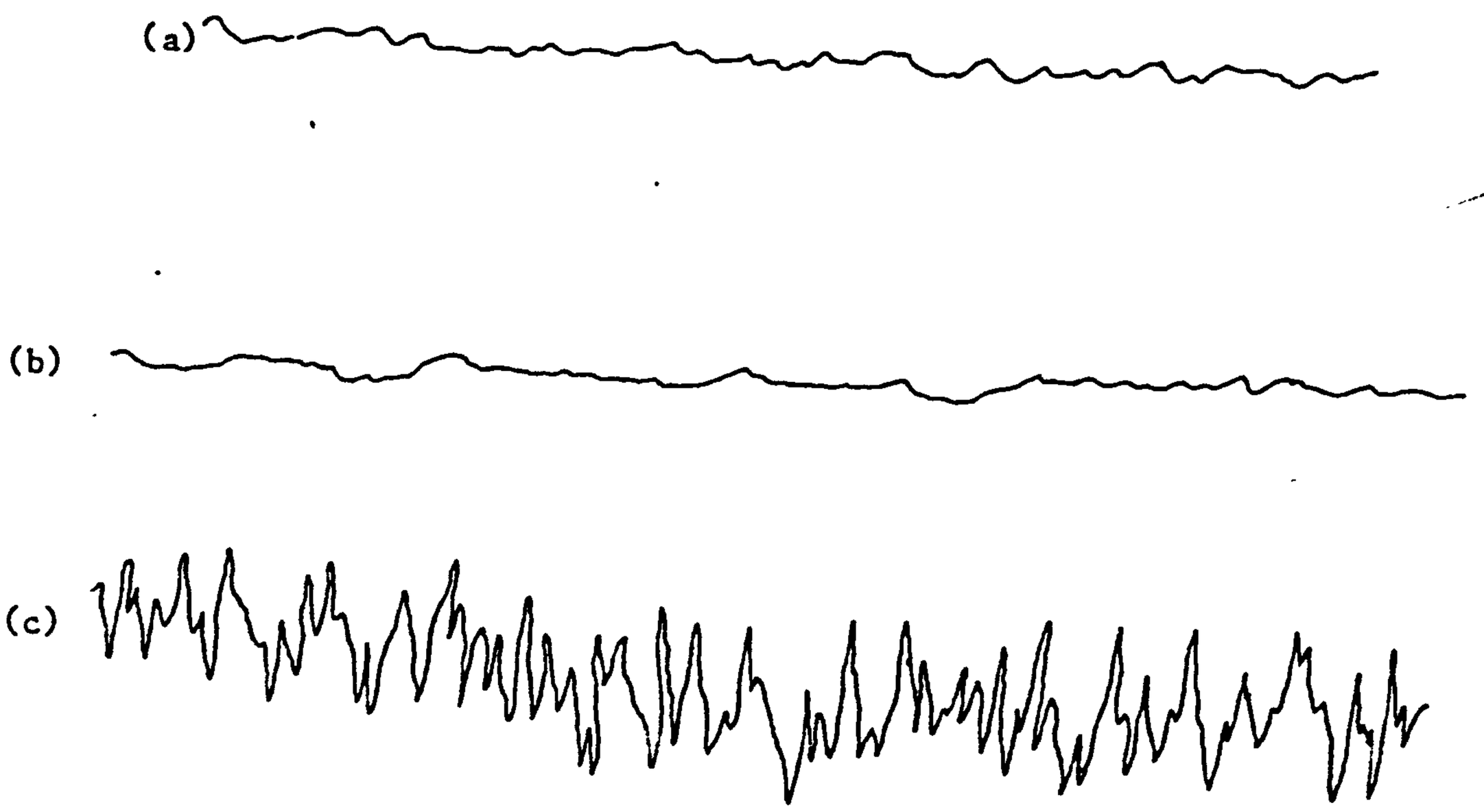


Fig.23
Talysurf profiles of chromic acid treated "Alkathene" WJG47.

Notes: (1) Horizontal magnification = 100X
Vertical magnification = 10,000X
(2) Curve (a) is for untreated "Alkathene" WJG47
(3) Curve (b) if for "Alkathene" WJG47 treated for 1 min. at 20°C.
(4) Curve (c) if for "Alkathene" WJG47 treated for 1h at 70°C

TABLE 5

Effect of extraction on chromic acid treated "Alkathene" WJG47

Material Extracted	Solvent	Time of Extraction	% original remaining
(a) Chromic acid treated "Alkathene" WJG47	Xylene	24h	1%
(b) Insoluble brown residue from (a)	50:50 aqueous ethanol	14d	0.7%
(c) Insolubles remaining from (b)	Dimethyl Formamide	6d	0.56%
(d) Insolubles remaining from (c)	Acetone	4d	0.52%

TABLE 6

Effect of very mild chromic acid and concentrated sulphuric acid treatment on polyolefins

Polymer	Conditions	C:S% atomic ratio	O:S % atomic ratio	%C with SO_3Hgps	% remaining O to total C	O1s:O2s ratio	Mean lap shear strength MNm^{-2}	Standard deviation	95% confidence limits	Type of failure
"Alkathene" WJG47	60 min in conc sulphuric acid at 70°C	36.7	3.8	2.7	2.1	11.6	2.34	0.19	0.1	I&M
"Alkathene" WJG47	5 secs in chromic acid at 20°C	19.8	11.0	0.5	4.0	-	4.79	1.08	0.7	M
"Rigidex" 50	60 min in conc sulphuric acid at 70°C	64.3	14.7	1.6	2.9	18.2	3.47	0.29	0.2	I&M
"Rigidex" 50	5 secs in chromic acid at 20°C	14.5	10.9	0.7	5.4	25.1	7.02	0.26	0.2	M
"Propathene" HF 20	60 min in conc sulphuric acid at 70°C	26.2	11.4	0.4	3.2	-	1.09	0.09	0.06	I
"Propathene" HF 20	5 secs in chromic acid at 20°C	38.2	17.2	0.3	3.7	35.9	2.79	0.58	0.4	M&I

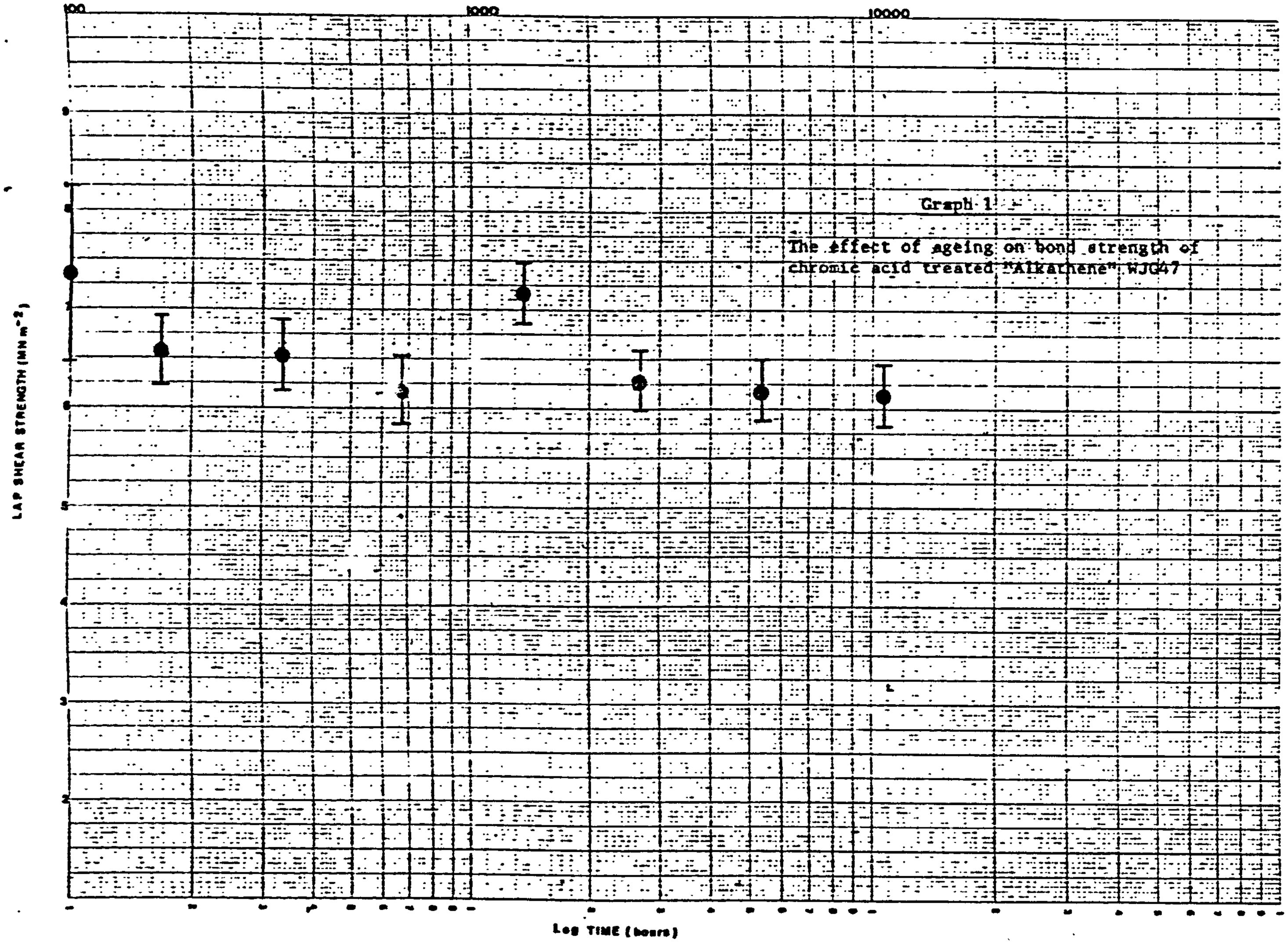
Notes: Chromic acid composition = $K_2Cr_2O_7$: H_2O : H_2SO_4 = 0.07 : 12:150 parts by weight

TABLE 7

Effect of ageing on bond strength of chromic acid treated "Alkathene" WJG47

Details of Treatment	Lap Shear Strengths MN m^{-2}	Mean	Standard Deviation	95% Confidence Limits	Contact angle θ^{o} adv	Type of Failure
a) Tested within 10h of treatment	3.10; 5.17; 7.58; 7.58; 8.96; 7.24; 6.89; 8.62; 8.27; 8.62; 8.27; 8.27; 8.27; 8.27; 7.93; 4.48.	7.35	1.67	0.9	76	M
b) Conditions as (a) but tested 7d later	6.89; 7.17; 7.34; 6.06; 6.34; 6.62; 7.79; 6.48; 7.24; 5.79; 6.34; 6.07; 6.34; 5.86; 6.21.	6.57	0.59	0.3	75	M
c) Conditions as (a) but tested 14d later	8.27; 6.89; 6.48; 5.93; 6.62; 6.34; 6.14; 6.34; 7.17; 5.86; 6.89; 6.06; 5.79; 7.17; 6.21.	6.54	0.65	0.4	76	M
d) Conditions as (a) but tested 28d later	4.41; 6.34; 6.48; 6.89; 6.62; 5.79; 7.03; 6.07; 6.21; 6.07; 6.48; 6.62; 5.24; 6.07; 6.21.	6.17	0.66	0.4	76	M
e) Conditions as (a) but tested 56d later	7.34; 7.34; 8.27; 7.34; 7.34; 7.34; 6.55; 7.79; 6.89; 6.76; 6.89; 7.34; 6.21; 7.34; 6.62.	7.16	0.52	0.3	79	M
f) Conditions as (a) but tested 112d later	6.14; 6.41; 6.07; 6.00; 5.24; 6.62; 6.62; 7.24; 6.21; 6.07; 7.03; 6.07; 5.45; 7.03; 5.93.	6.28	0.56	0.3	77	M
g) Conditions as (a) but tested 224d later	6.14; 5.65; 6.55; 6.07; 6.83; 6.21; 5.10; 6.62; 6.48; 6.14; 6.07; 6.07; 5.65; 6.96; 6.27.	6.19	0.48	0.3	76	M
h) Conditions as (a) but tested 448d later	6.14; 6.14; 6.48; 6.14; 5.93; 6.27; 6.55; 7.03; 5.38; 6.55; 6.69; 5.24; 6.69; 5.52; 5.38	6.14	0.55	0.3	77	M

Notes: (1) 1 min. in chromic acid at $20^{o}C$
(2) Chromic acid composition $K_2Cr_2O_7 : H_2O : H_2SO_4 = 7:12:150$
(3) Both sides treated.



Graph 1

The effect of ageing on bond strength of chromic acid treated "Alkathene" WJG47

TABLE 8

XPS and joint strength data for flame treated polyethylenes

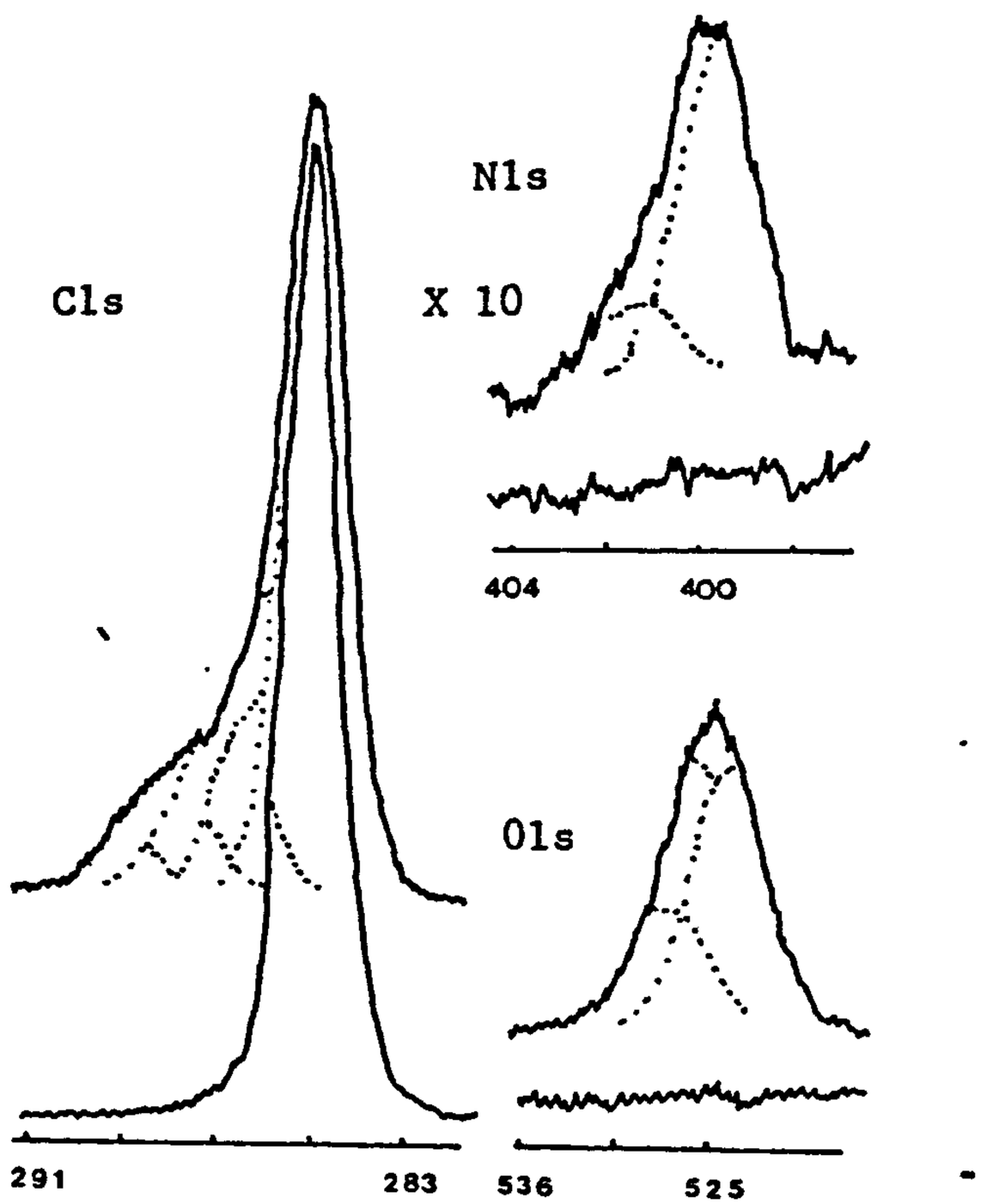
Polymer	Treatment time (sec)	Natural gas flow ($cm^3 sec^{-1}$)	Air flow ($cm^3 sec^{-1}$)	O:C (at %)	N:C (at %)	Lap shear strength[3] (MNm^{-2})	Standard Deviation	95% confidence limits
a. "Alkathene" 47 [1]	0	0	0	0.25	0	0.55	0.07	0.05
b. "Alkathene" 47	1.2	37	150	16.9	0.94	6.6	0.6	0.41
c. "Alkathene" 47	4.8	37	150	31.0	3.2	7.2	0.7	0.53
d. "Alkathene" 47	1.2	74	317	15.3	2.2	6.8	0.7	0.51
e. "Alkathene" 47	1.2	18.5	75	6.8	0	5.1	0.6	0.44
f. "Alkathene" 11 [2]	0	0	0	<0.25	0	0.36	0.04	0.03
g. "Alkathene" 11	1.2	37	150	20.5	1.5	5.6	0.5	0.39
h. "Alkathene" 11	4.8	37	150	33.4	3.2	7.2	0.4	0.27
i. "Alkathene" 11	1.2	74	317	13.7	2.5	6.4	0.3	0.22
j. "Alkathene" 11	1.2	18.5	75	5.1	0	5.7	0.4	0.28

Notes:
(1) Contains no additives.
(2) Contains 0.02% 2,6-ditert-butyl-p-cresol
(3) With the treated polymers the failure was always a mixture of apparent interfacial and material.
(4) After 390d "Alkathene" WJG47 treated as a. gave a mean lap shear strength of 6.34; standard deviation of 0.6 and 95% confidence limits of 0.43.
(5) After 390d "Alkathene" WJG11 treated as g. gave a mean lap shear strength of 5.45; standard deviation of 0.5 and 95% confidence limits of 0.37.

Spectrum 4.

Core level spectra (on Binding energy scale) from "Alkathene" WJG11

lower trace - untreated
upper trace - after 4X normal flame treatment.

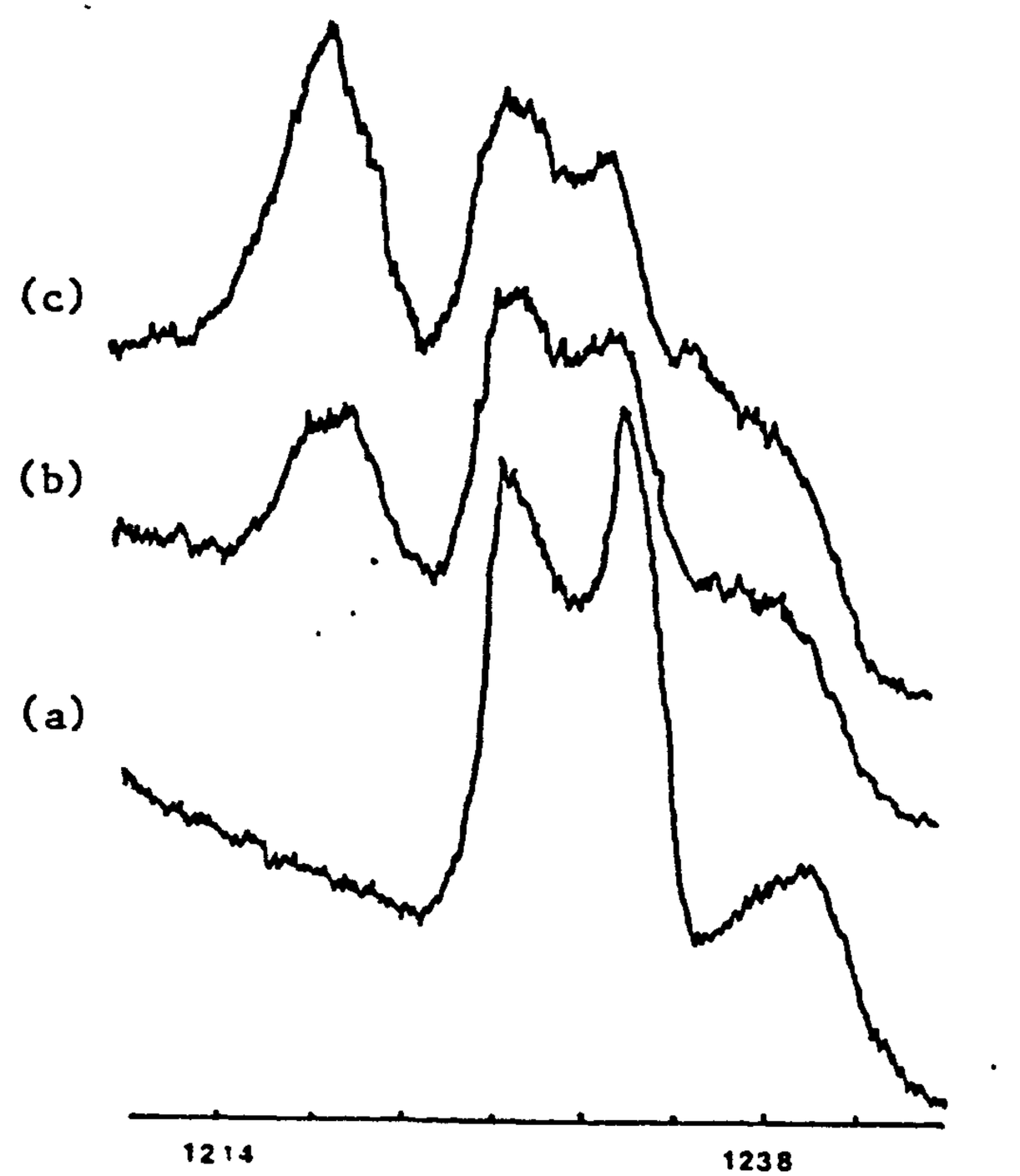


Binding Energy eV.

Spectrum 5.

Valence band spectra from "Alkathene" WJG11.

(a) Untreated
(b) After normal flame treatment
(c) After 4X normal flame treatment



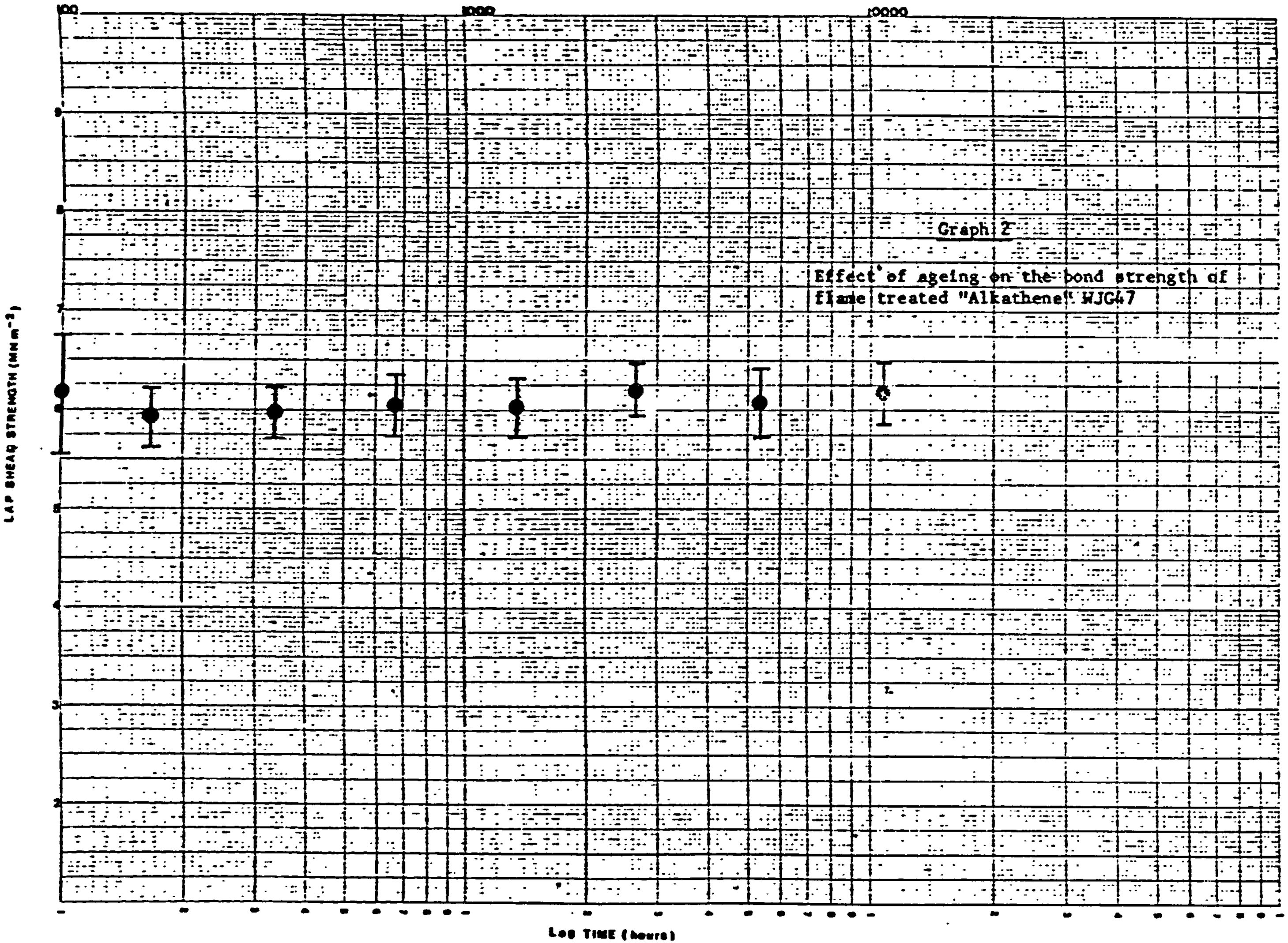
Kinetic Energy eV.

TABLE 9

Effect of ageing on the bond strength of flame treated "Alkathene" WJG47

Details of Treatment	Lap Shear Strengths $MN\ m^{-2}$	Mean	Standard Deviation	95% Confidence Limits	Contact angle θ_{adv}	Type o Failur
a) Tested within 10h of treatment	7.72; 8.27; 7.03; 7.03; 8.00; 8.27; 6.62; 6.34; 6.34; 7.10; 6.69; 8.00; 6.62; 6.89; 7.45.	7.24	0.67	0.4	61	M
b) Conditions as (a) but tested 7d later	7.45; 7.17; 6.62; 6.34; 6.89; 5.93; 6.89; 7.17; 6.07; 6.34; 6.34; 6.55; 6.07; 5.79; 6.89.	6.57	0.50	0.3	61	M
c) Conditions as (a) but tested 14d later	6.89; 6.07; 7.45; 6.62; 7.17; 5.93; 5.52; 6.76; 6.34; 7.45; 7.45; 6.62; 5.79; 7.17; 6.07.	6.62	0.65	0.4	60	M
d) Conditions as (a) but tested 28d later	6.79; 7.21; 7.21; 6.93; 7.41; 6.24; 5.83; 5.83; 7.55; 6.79; 6.10; 6.93; 7.07; 5.96; 6.93.	6.72	0.58	0.3	64	M
e) Conditions as (a) but tested 56d later	7.21; 6.93; 7.00; 6.24; 7.34; 6.38; 6.10; 7.07; 6.17; 6.31; 6.38; 7.07; 6.31; 7.07; 7.00	6.71	0.44	0.2	63	M
f) Conditions as (a) but tested 112d later	6.24; 5.83; 6.93; 5.69; 6.93; 6.52; 6.31; 5.83; 6.18; 6.38; 6.18; 6.10; 6.52; 6.24; 5.83.	6.25	0.38	0.2	62	M
g) Conditions as (a) but tested 224d later	6.18; 5.96; 6.31; 6.10; 5.83; 6.24; 6.24; 5.90; 6.10; 6.10; 6.58; 5.83; 6.17; 5.69; 6.38	6.11	0.24	0.1	64	M
h) Conditions as (a) but tested 448d later	6.48; 7.10; 5.17; 6.24; 6.17; 6.24; 5.69; 6.76; 6.76; 5.69; 5.96; 6.92; 6.83; 6.24; 6.92.	6.34	0.55	0.3	63	M

Notes: 1. Flame treatment, 3.2 sec in gas/air flame. Gas flow = $37cm^3\ sec^{-1}$. Air flow = $37cm^3\ sec^{-1}$.
2. Films treated both sides.
3. Film to nozzle distance = 50mm.



Graph 2

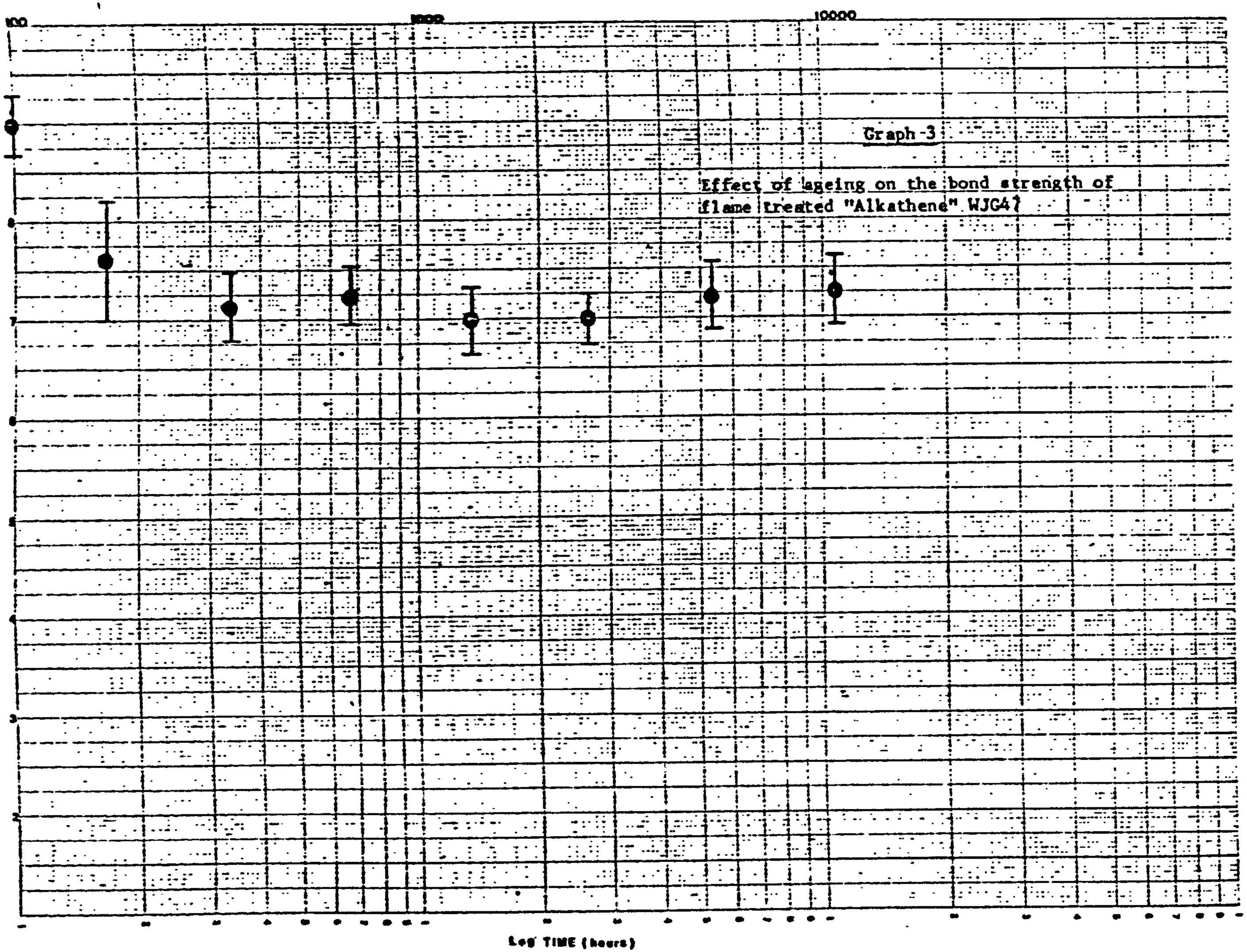
Effect of ageing on the bond strength of flame treated "Alkathene" WJG47

TABLE 10

Effect of ageing on the bond strength of flame treated "Alkathene" WJG47

Details of Treatment	Lap Shear Strengths $MN\ m^{-2}$	Mean	Standard Deviation	95% Confidence Limits	Contact angle θ_{adv}	Type of Failure
a) Tested within 10h of treatment	8.83; 9.45; 8.76; 7.72; 9.10; 9.65; 9.78; 8.83; 9.24; 9.37; 8.96; 8.55; 8.27; 9.31.	8.99	0.516	0.31	66	M
b) Conditions as (a) but tested 7d later	8.27; 8.83; 7.72; 8.27; 8.14; 8.14; 8.83; 7.31; 5.65; 5.65; 6.76; 7.10; 8.14; 7.72.	7.61	1.02	0.6	66	M
c) Conditions as (a) but tested 14d later	6.21; 6.76; 7.10; 6.89; 6.34; 7.72; 8.00; 7.45; 6.34; 7.17; 7.10; 7.72; 6.89; 8.14	7.13	0.62	0.4	66	M
d) Conditions as (a) but tested 28d later	7.31; 6.89; 8.00; 7.17; 6.62; 7.31; 7.03; 7.31; 7.45; 7.72; 6.89; 6.62; 6.62; 8.27.	7.23	0.51	0.3	67	M
e) Conditions as (a) but tested 56d later	7.72; 6.89; 6.69; 6.69; 7.58; 6.76; 7.58, 7.92; 6.48; 6.21; 6.89; 6.76; 6.07; 7.58.	6.99	0.59	0.3	65	M
f) Conditions as (a) but tested 112d later	6.76; 7.17; 6.48; 6.48; 7.72; 6.89; 6.89; 7.17; 7.03; 6.89; 6.62; 6.89; 7.92; 7.03.	7.00	0.41	0.2	66	M
g) Conditions as (a) but tested 224d later	6.89; 7.92; 7.72; 7.72; 6.89; 7.45; 6.34; 8.14; 6.21; 7.31; 7.03; 6.48; 7.65; 7.38	7.22	0.60	0.4	67	M
h) Conditions as (a) but tested 448d later	7.72; 7.72; 7.92; 7.45; 7.86; 6.89; 8.00; 6.48; 6.35; 7.86; 6.89; 6.69; 6.76; 7.17	7.27	0.59	0.3	65	M

Notes:
1. Flame treatment 0.8 sec in gas/air flame. Gas flow = $62cm^3\ sec^{-1}$. Air flow = $404cm^3\ sec^{-1}$
2. Treatment both sides.
3. Film to nozzle distance = 50mm.



Graph 3

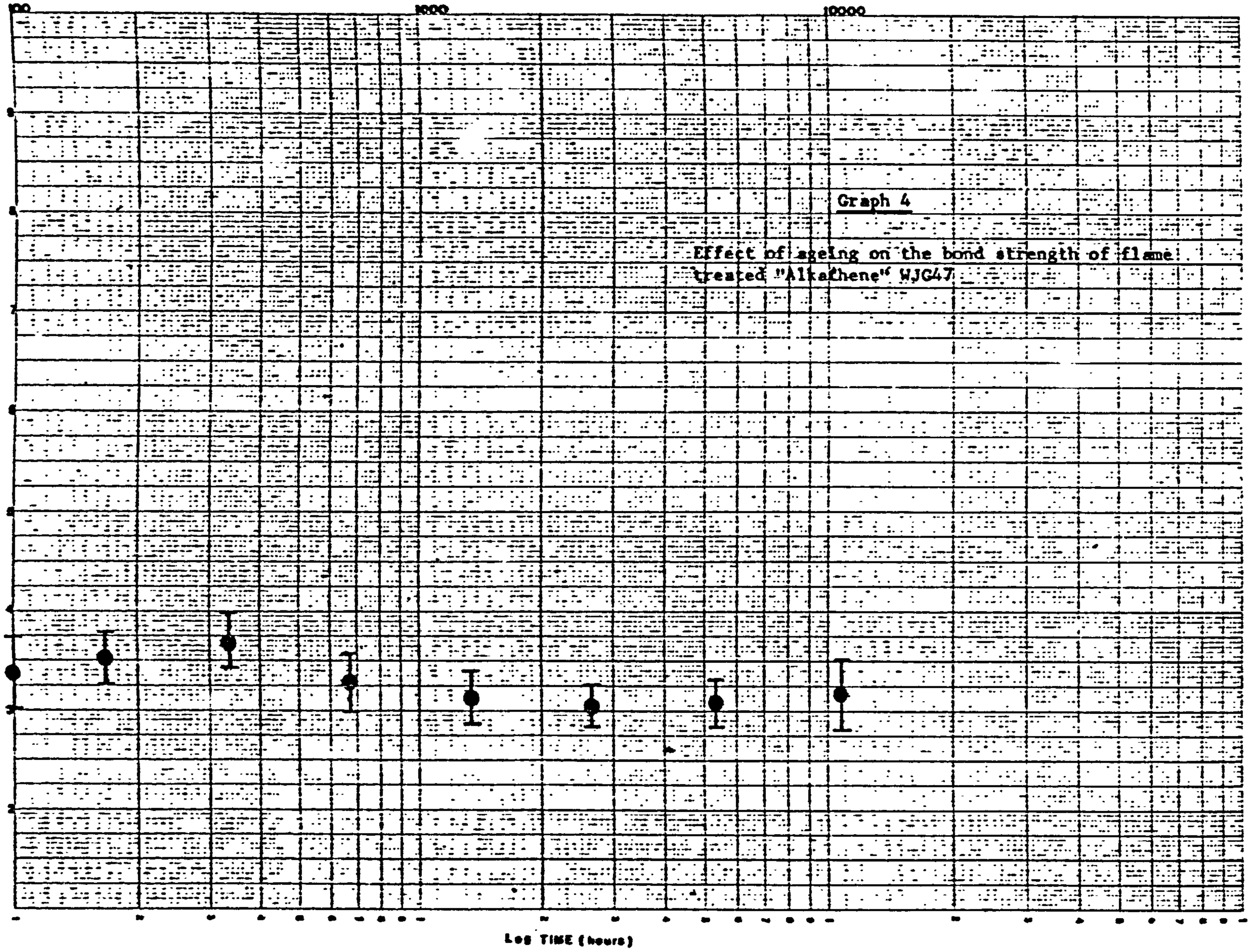
Effect of ageing on the bond strength of flame treated "Alkathene" WJC47

TABLE 11

Effect of ageing on the bond strength of flame treated "Alkathene" WJG47

Details of Treatment	Lap Shear Strengths $MN\ m^{-2}$	Mean	Standard Deviation	95% Confidence Limits	Contact angle θ adv	Type of Failure
a) Tested within 10h of treatment	3.31; 2.62; 3.72; 3.72; 3.03; 3.45; 4.76; 3.59; 3.45; 2.90; 3.45; 2.76; 4.41; 2.69; 2.76.	3.37	0.62	0.4	77	M
b) Conditions as (a) but tested 7d later	3.72; 2.90; 3.03; 3.03; 4.41; 3.37; 4.14; 3.59; 3.45; 3.03; 3.45; 3.59; 3.72; 4.14; 3.37.	3.53	0.45	0.3	76	M
c) Conditions as (a) but tested 14d later	3.31; 2.90; 3.86; 3.45; 3.45; 3.72; 4.69; 3.45; 4.55; 3.45; 4.00; 3.45; 3.79; 3.52; 3.72.	3.69	0.46	0.3	77	M
d) Conditions as (a) but tested 28d later	3.31; 3.08; 3.86; 3.45; 3.17; 3.79; 4.14; 3.45; 2.76; 2.46; 2.41; 2.62; 3.73; 3.59; 3.45.	3.28	0.53	0.3	76	M
e) Conditions as (a) but tested 56d later	3.72; 3.45; 2.76; 3.24; 2.76; 3.03; 3.03; 2.69; 3.59; 2.62; 2.69; 2.41; 3.72; 3.59; 3.45.	3.12	0.45	0.3	74	M
f) Conditions as (a) but tested 112d later	3.37; 3.31; 2.90; 3.10; 3.52; 2.69; 3.03; 2.69; 3.59; 3.03; 2.96; 2.96; 3.17; 2.41; 2.96.	3.05	0.32	0.2	76	M
g) Conditions as (a) but tested 224d later	2.76; 3.35; 2.62; 3.24; 2.34; 3.03; 3.03; 2.69; 3.59; 2.34; 3.31; 3.03; 3.72; 3.59; 3.45.	3.07	0.45	0.3	75	M
h) Conditions as (a) but tested 448d later	3.31; 3.03; 3.86; 3.45; 3.17; 3.79; 4.14; 3.45; 2.76; 2.41; 2.14; 2.62; 3.72; 2.34; 3.17.	3.16	0.60	0.3	76	M

Notes: 1. Flame treatment; 0.8 sec in gas/air flame.
Gas flow = $37cm^3\ sec^{-1}$. Air flow = $37cm^3\ sec^{-1}$
2. Films treated both sides.
3. Film to nozzle distance = 50mm.



Graph 4

Effect of ageing on the bond strength of flame treated "Alkathene" WJG47

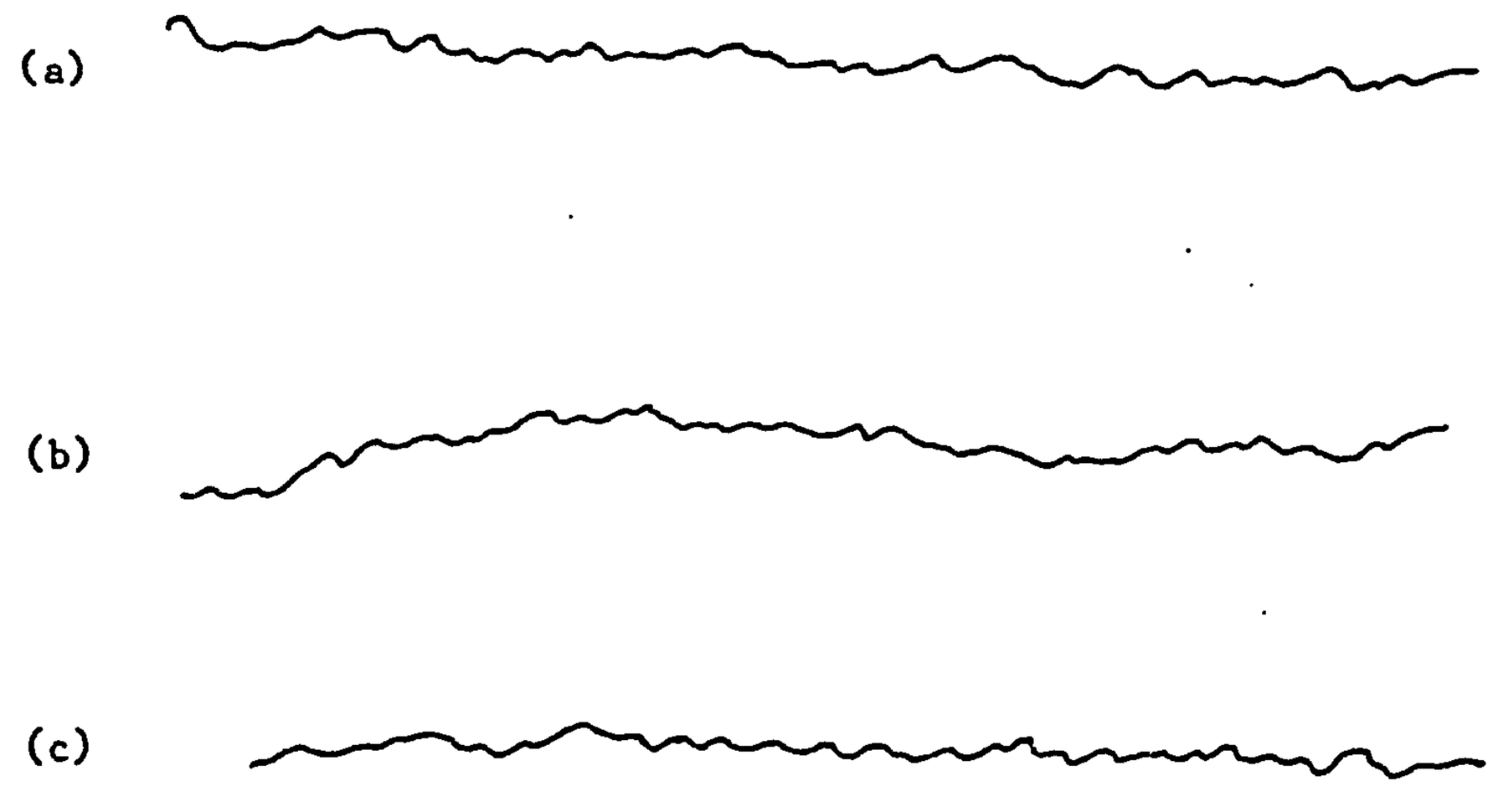
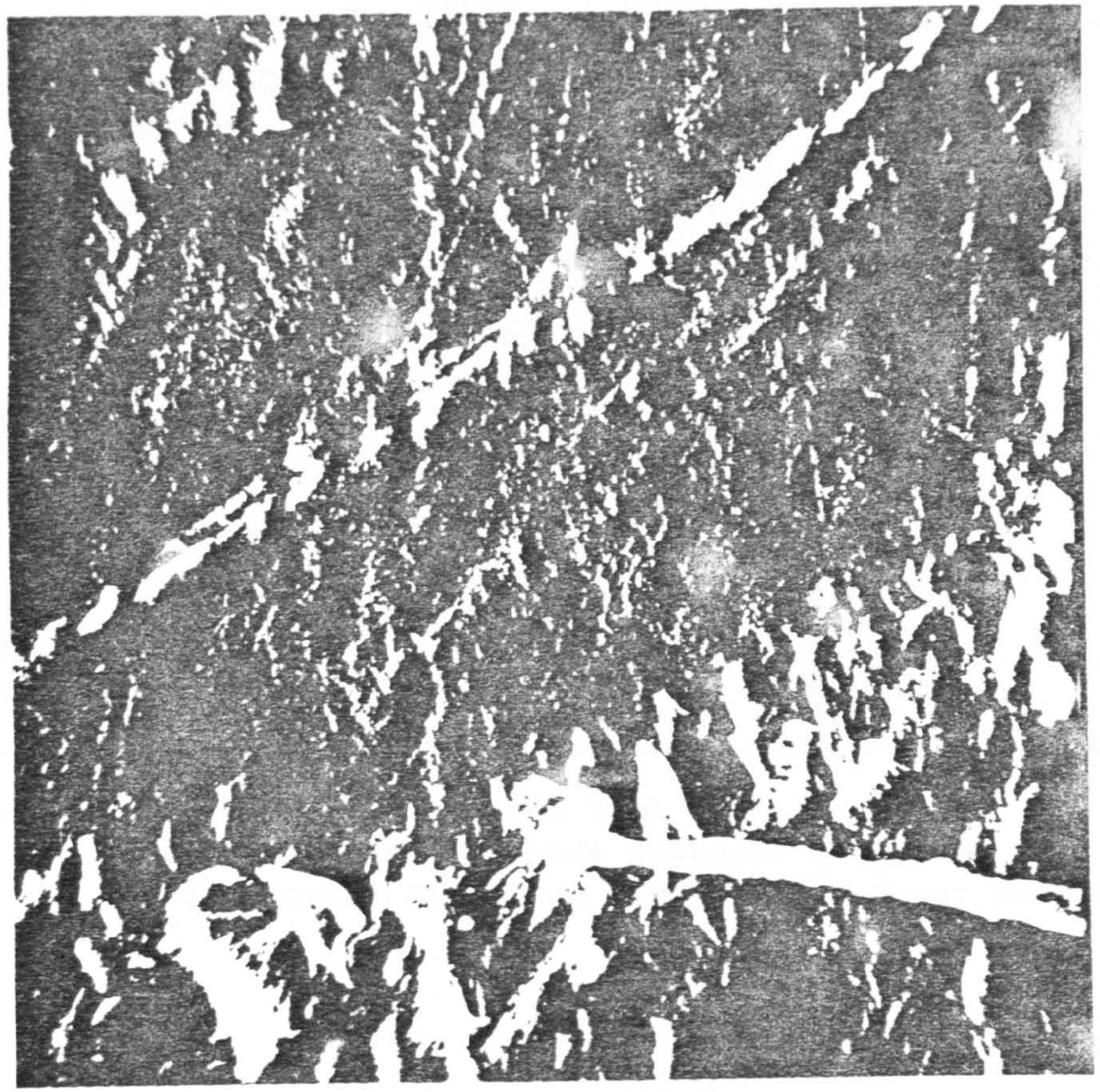


Fig.24
Talysurf profiles of flame treated "Alkathene" WJG47.

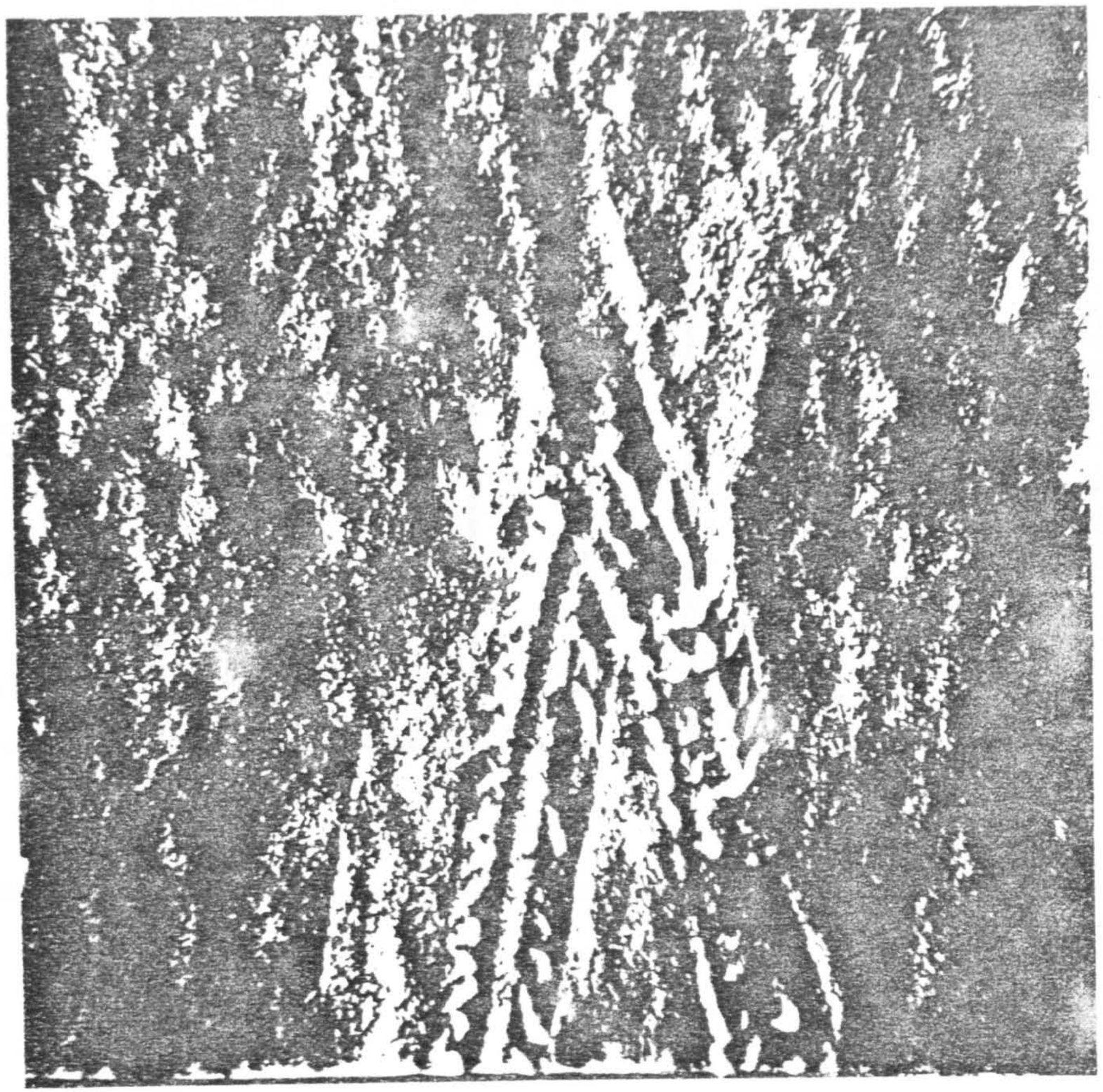
Notes: (1) Horizontal manification = 100X
Vertical magnification = 10,000X
(2) Curve (a) is for untreated "Alkathene" WJG47
(3) Curve (b) is for flame treated "Alkathene" WJG47. Treatment time 1.2 sec. Natural gas flow = 37 cm^3 sec^{-1}; air flow = 150 cm^3 sec^{-1}.
(4) Curve (c) is for flame treated "Alkathene" WJG47. Treatment time 4.8 sec. Natural gas flow = 37 cm^3 sec^{-1}; air flow = 150 cm^3 sec^{-1}.

Photo-micrograph 3.

Flame treated polyethylene.
a. Treatment conditions: 1.2 seconds in gas/air flame (flow rates 37 and 150 cm^3 sec^{-1} respectively).
b. Untreated, magnification 2100X.



a.



b.

TABLE 12

XPS Data & Joint strength values for Corona discharge treated polyolefins

Polymer	O:C % atomic ratio	N:C % atomic ratio	Mean lap shear strength MNm^{-2}	Standard Deviation	95% confidence limits	Contact angle θ adv.	Type of failure
"Alkathene" WJG47 untreated	0.25	0	0.55	0.07	0.05	98	I
"Alkathene" WJG47	11.1	1.22	6.07	0.67	0.5	64	M
"Alkathene" WJG11 untreated	<0.25	0	0.36	0.13	0.09	86	I
"ALkathene" WJG11 treated	14.5	1.42	8.14	0.36	0.2	51	M
"Propathene" HF20 untreated	0.25	0	0.28	0.01	0.04	92	I
"Propathene" HF20 treated	14.6	1.38	1.24	0.14	0.09	76	I&M

Notes: (1) Samples treated both sides.
(2) Film to electrode distance = 1.524mm
(3) Corona discharge conditions. Power output = 180 watts. Haul off speed = 0.13mm sec^{-1}.

TABLE 13

XPS Data and Joint Strengths for Corona Treated Polyolefins

Polymer	Treatment details	O1s:C1s Peak Ratio	Mean lap shear strength MNm^{-2}	Standard Deviation	95% Confidence limits	Type of failure
"Alkathene" WJG47	Power Output = 340 watts, Haul off speed = 0.3m sec^{-1}	-	4.93	0.30	0.2	M
"Alkathene" WJG47	Power Output = 240 watts, Haul off speed = 0.3m sec^{-1}	-	6.80	0.47	0.3	M
"Alkathene" WJG47	Power Output = 150 watts, Haul off speed = 0.3m sec^{-1}	0.74	6.96	0.61	0.4	M
"Alkathene" WJG47	Power Output = 90 watts, Haul off speed = 0.3m sec^{-1}	-	7.52	0.34	0.2	M
"Alkathene" WJG47	Power Output = 150 watts Haul off speed = 0.4 sec^{-1}	-	7.31	0.4	0.3	M
"Alkathene" WJG47	Power Output = 150 watts, Haul off speed = 0.2m sec^{-1}	-	6.14	0.79	0.5	M
"Alkathene" WJG11	Power Output = 150 watts, Haul off speed = 0.3m sec^{-1}	0.78	7.08	0.50	0.3	M
"Propathene" HF20	Power output = 150 watts, Haul off speed = 0.3m sec^{-1}	0.44	2.48	0.52	0.4	I

Notes: (1) I = apparent interfacial failure.
M = failure in the polyolefin

(11) Samples treated one side only - other side treated with chromic acid

(a)

(b)

Fig.25
Talysurf profiles of corona discharge treated "Alkathene" WJG47.

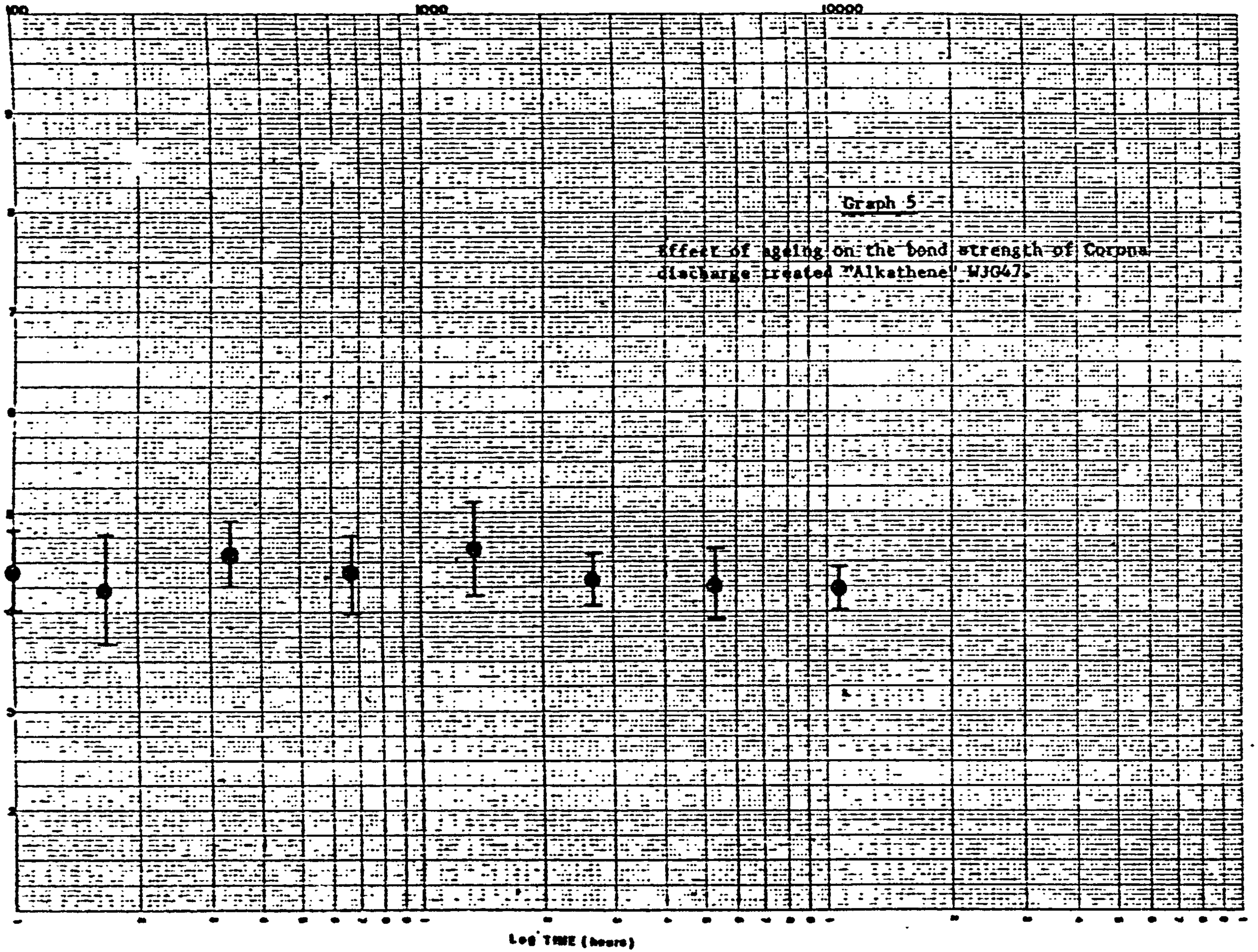
Notes: (1) Horizontal magnification = 100X
Vertical magnification = 10,000X
(2) Curve (a) is for untreated "Alkathene" WJG47
(3) Curve (b) is for corona discharge treated "Alkathene" WJG47.
Treatment conditions:- Power output - 180 watts
Haul off speed - 0.13 m sec^{-1}

TABLE 14

Effect of ageing on the bond strength of Corona treated "Alkathene" WJG47

Details of Treatment	Lap Shear Strengths $MN\ m^{-2}$	Mean	Standard Deviation	95% Confidence Limits	Contact angle θ adv	Type of Failure
a) Tested within 10h of treatment	3.50; 5.21; 3.90; 3.90; 4.80; 5.21; 5.31; 3.90; 3.90; 4.69; 5.24; 4.83; 3.50; 3.90.	4.41	.0.687	0.4	66	M
b) Conditions as (a) but tested 7d later	4.41; 3.31; 4.14; 3.62; 3.50; 3.03; 4.52; 5.00; 4.00; 5.79; 3.50; 3.34; 5.44; 5.65.	4.23	0.928	0.5	67	M
c) Conditions as (a) but tested 14d later	5.38; 4.55; 5.10; 3.50; 4.27; 4.96; 5.38; 4.14; 4.27; 4.96; 4.14; 3.86; 4.55; 4.83.	4.56	0.566	0.3	66	M
d) Conditions as (a) but tested 28d later	4.67; 3.31; 3.79; 5.52; 4.14; 3.03; 4.96; 3.86; 5.59; 4.69; 5.38; 4.14; 4.69; 3.59.	4.38	0.818	0.5	66	M
e) Conditions as (a) but tested 56d later	5.52; 3.03; 5.52; 4.69; 3.31; 5.65; 4.00; 3.93; 4.83; 4.83; 5.48; 4.41; 4.76; 4.76.	4.62	0.818	0.5	68	M
f) Conditions as (a) but tested 112d later	4.83; 4.27; 4.69; 4.00; 4.83; 5.10; 4.14; 4.69; 3.72; 3.86; 4.27; 4.14; 4.27; 3.60.	4.32	0.453	0.3	70	M
g) Conditions as (a) but tested 224d later	4.00; 3.93; 5.24; 5.17; 4.14; 4.14; 3.95; 3.72; 3.72; 3.72; 5.35; 5.03; 4.00; 3.72.	4.27	0.626	0.4	72	M
h) Conditions as (a) but tested 448d later	3.93; 4.41; 3.60; 4.14; 4.41; 4.96; 4.14; 3.93; 3.72; 4.14; 4.14; 4.69; 4.27; 4.41;	4.23	0.364	0.2	70	M

Notes:
1. Power output = 440 watts; haul off speed = 0.45m sec^{-1}
2. Treatment both sides
3. Distance of electrode to film = 1.524mm
4. (a) is said to give satisfactory results for printing.



Graph 5

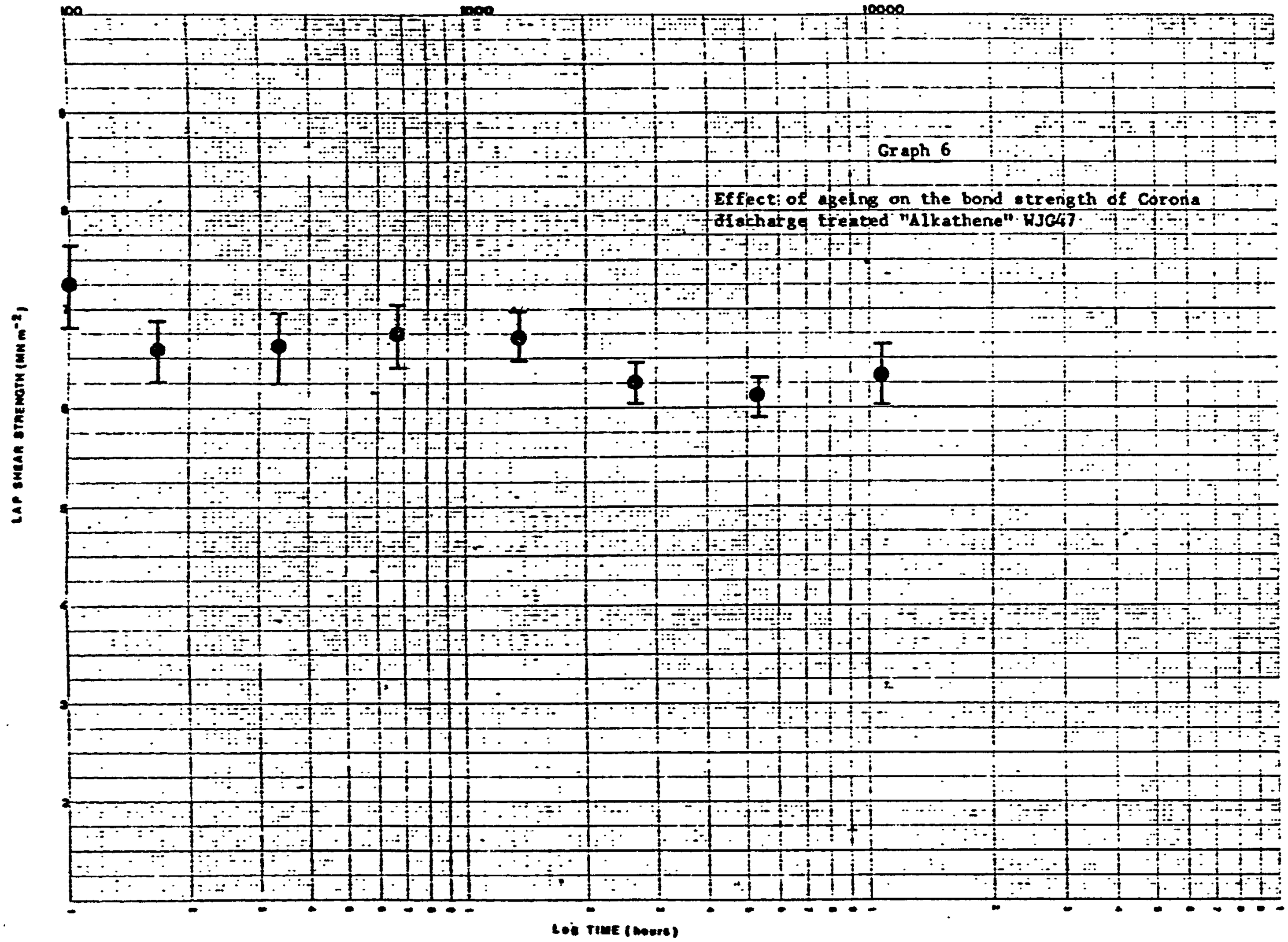
Effect of ageing on the bond strength of Corona discharge treated "Alkathene" WJG47.

TABLE 15

Effect of ageing on the bond strength of Corona treated "Alkathene" WJG47

Details of Treatment	Lap Shear Strengths MN m^{-2}	Mean	Standard Deviation	95% Confidence Limits	Contact angle θ adv	Type of Failure
a) Tested within 10h of treatment	4.14; 5.58; 6.34; 6.34; 7.17; 6.34; 7.24; 7.45; 7.45; 5.45; 6.34; 6.34; 5.52; 4.48.	6.16	1.03	0.6	66	M
b) Conditions as (a) but tested 7d later	5.58; 5.65; 6.14; 5.65; 6.14; 5.38; 5.52; 5.24; 7.07; 6.59; 5.58; 6.00; 6.14; 6.52.	5.94	0.52	0.3	68	M
c) Conditions as (a) but tested 14d later	5.65; 6.14; 6.55; 5.65; 5.72; 5.72; 5.52; 6.83; 5.86; 6.00; 5.72; 6.14; 5.72; 6.55.	5.98	0.41	0.2	66	M
d) Conditions as (a) but tested 28d later	6.48; 5.38; 5.52; 5.38; 6.69; 6.14; 5.65; 5.52; 6.14; 6.69; 6.83; 6.14; 6.00; 6.14.	6.05	0.50	0.3	66	M
e) Conditions as (a) but tested 56d later	5.48; 6.14; 5.10; 5.79; 6.69; 6.55; 6.14; 6.34; 6.21; 5.24; 6.14; 5.79; 6.14; 6.69.	6.03	0.50	0.3	68	M
f) Conditions as (a) but tested 112d later	5.65; 6.14; 5.93; 6.14; 6.55; 6.62; 6.41; 6.69; 5.79; 6.00; 6.27; 5.52; 6.27; 6.69.	6.19	0.38	0.3	69	M
g) Conditions as (a) but tested 224d later	5.65; 6.82; 6.55; 5.79; 6.27; 5.93; 5.10; 6.55; 6.14; 5.10; 5.86; 6.96; 5.38; 6.69.	6.06	0.62	0.4	70	M
h) Conditions as (a) but tested 448d later	5.60; 5.45; 6.41; 6.27; 6.69; 5.79; 6.89; 6.69; 5.79; 5.65; 5.86; 6.41; 6.89; 5.79.	6.16	0.51	0.3	68	M

Notes: 1. Power output = 440 watts; haul off speed = 0.23m sec^{-1}
2. Treated both sides.
3. Distance of electrode to film = 1.524mm.



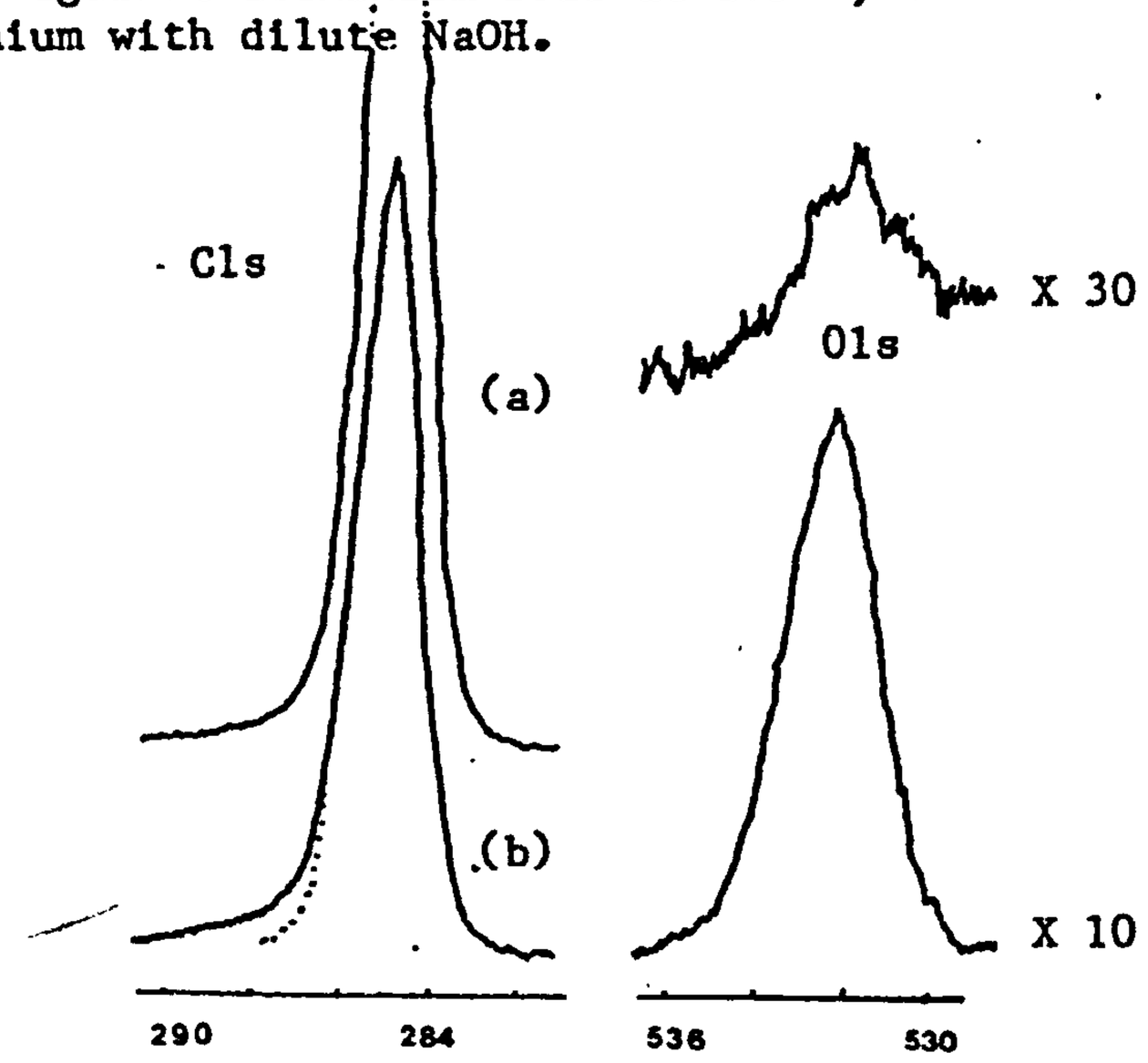
Graph 6

Effect of ageing on the bond strength of Corona discharge treated "Alkathene" WJG47

Spectrum 6.

Cls and Ols peaks from low density polyethylene.

(a) Untreated
(b) Melted against aluminium foil at 175°C, followed by dissolution of aluminium with dilute NaOH.



Binding Energy eV

TABLE 16

XPS data, joint strengths and advancing contact angles for polyethylenes that have been melted against aluminium or poly(ethylene terephthalate).

Polymer	Substrate	Temperature °C	O:C atomic %	Mean lap shear strength MNm^{-2}	Standard deviation	95% confidence limits	Type of failure	θ adv. deg.
"Rigidex" 50	Poly(ethylene terephthalate)	150	0.52	0.38	0.03	0.02	I	96
"Rigidex" 50	Aluminium	150	6.20	1.43	0.22	0.1	I	85
"Rigidex" 50	Aluminium	175	+	2.19	0.28	0.2	I	93
"Rigidex" 50 Peeled	Aluminium	150	0.92	-	-	-	-	-
"Alkathene" WJG47	Poly(ethylene terephthalate)	150	0.25	0.55	0.05	0.03	I	98
"Alkathene" WJG47	Aluminium	150	3.75	5.65	0.69	0.4	M	78
"Alkathene" WJG47	Aluminium	175	6.88	6.38	0.55	0.3	M	80

* The polymers were pressed against the substrate for 10 minutes at the temperatures stated.

\+ Not available, see test.

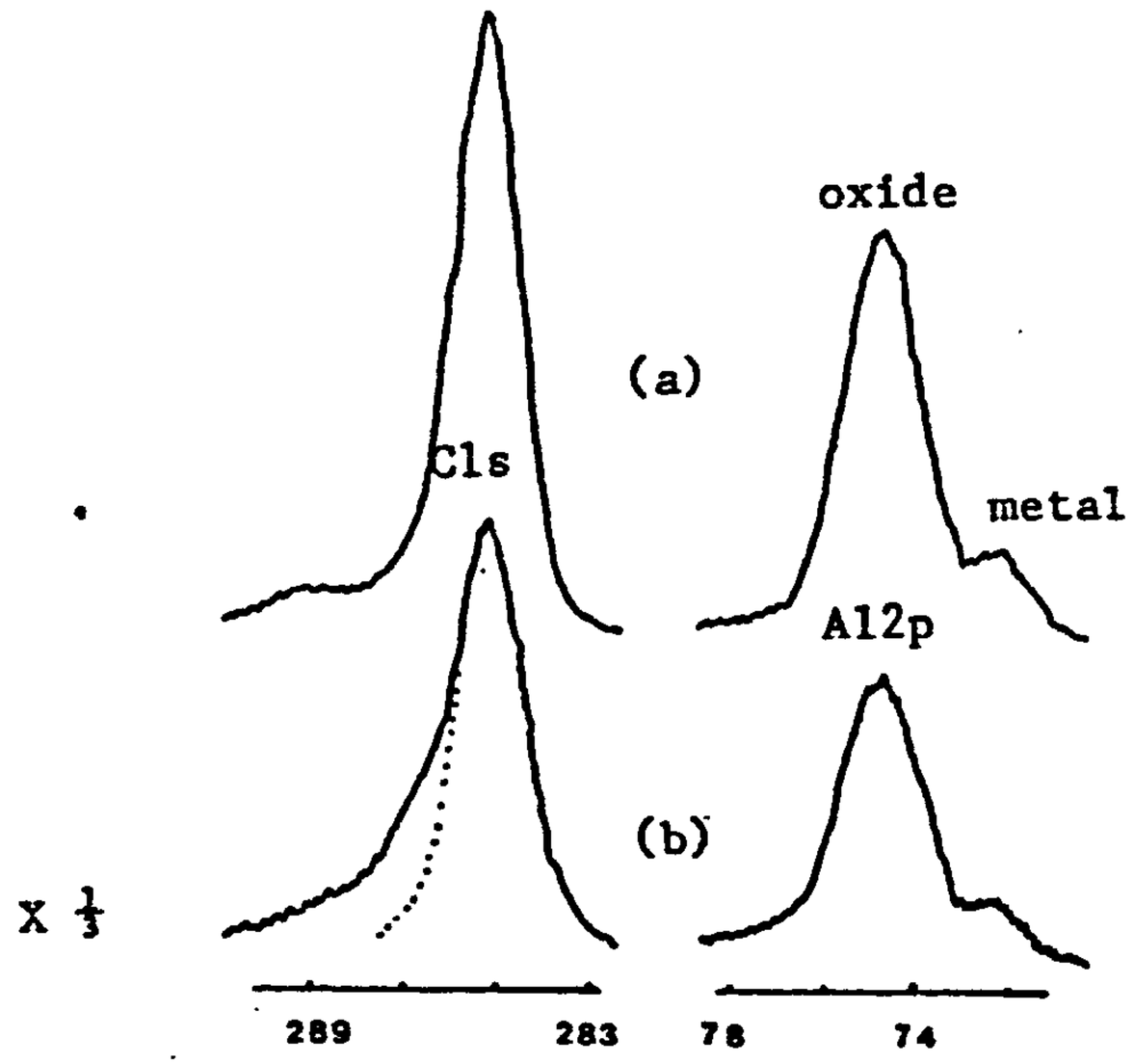
I ..... apparent interfacial failure.

M ..... failure of the polyethylene.

Spectrum 7.

C1s and A12p peaks from aluminium foil.

(a) "Clean" foil.
(b) Foil surface resulting from peeling at the aluminium foil/high density polyethylene interface.



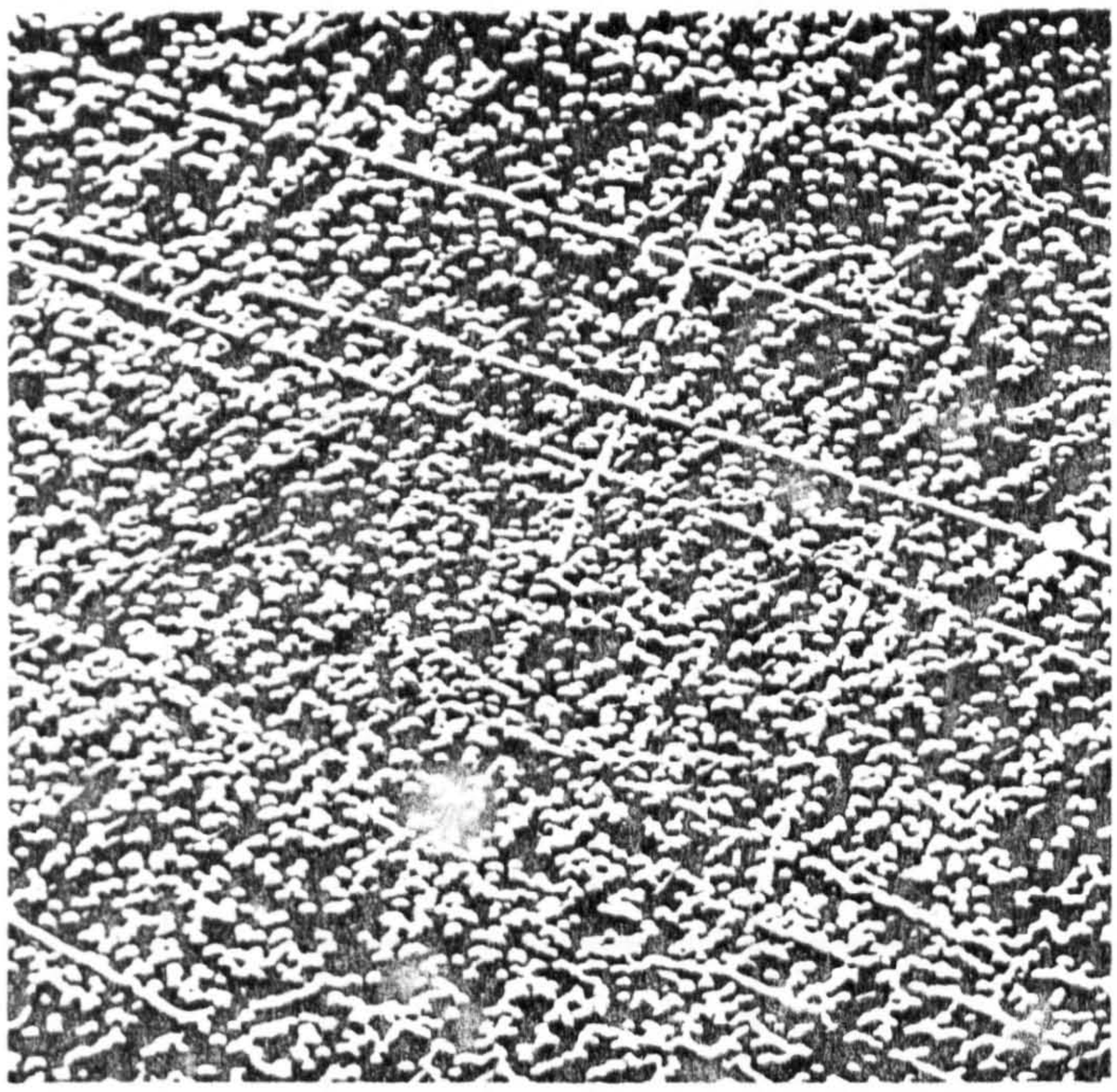
Binding energy eV

TABLE 17

Estimation of unsaturation from XPS data on bromine uptake

Polymer	Substrate	Temperature °C	CIS ($^{I}CH_2$)*	Br3d^{+}	Ic=c$^{\neq}$	Ic=c:I_{CH2} (%)
"Alkathene" WJG47	Polyethylene terephthalate	150	22.3	0.31	0.16	0.7
"Alkathene" WJG47	Aluminium	150	21.0	0.80	0.40	1.9
"Rigidex" 50	Polyethylene terephthalate	150	22.3	0.04	0.02	0.01
"Rigidex" 50	Aluminium	150	20.1	0.38	0.19	0.9

Notes:
* Peak height (arbitrary units)
+ Corrected for relative photoemission cross-section.
≠ Ic=c = Br3d/2 since >C = C< + Br_2 → >CBr-CBR<



a.

b.

Photo-micrograph 4.

Polyethylene after nucleation in contact with aluminium. Aluminium removed by dissolution.

(a) Magnification 210X
(b) Magnification 2,100X

TABLE 18

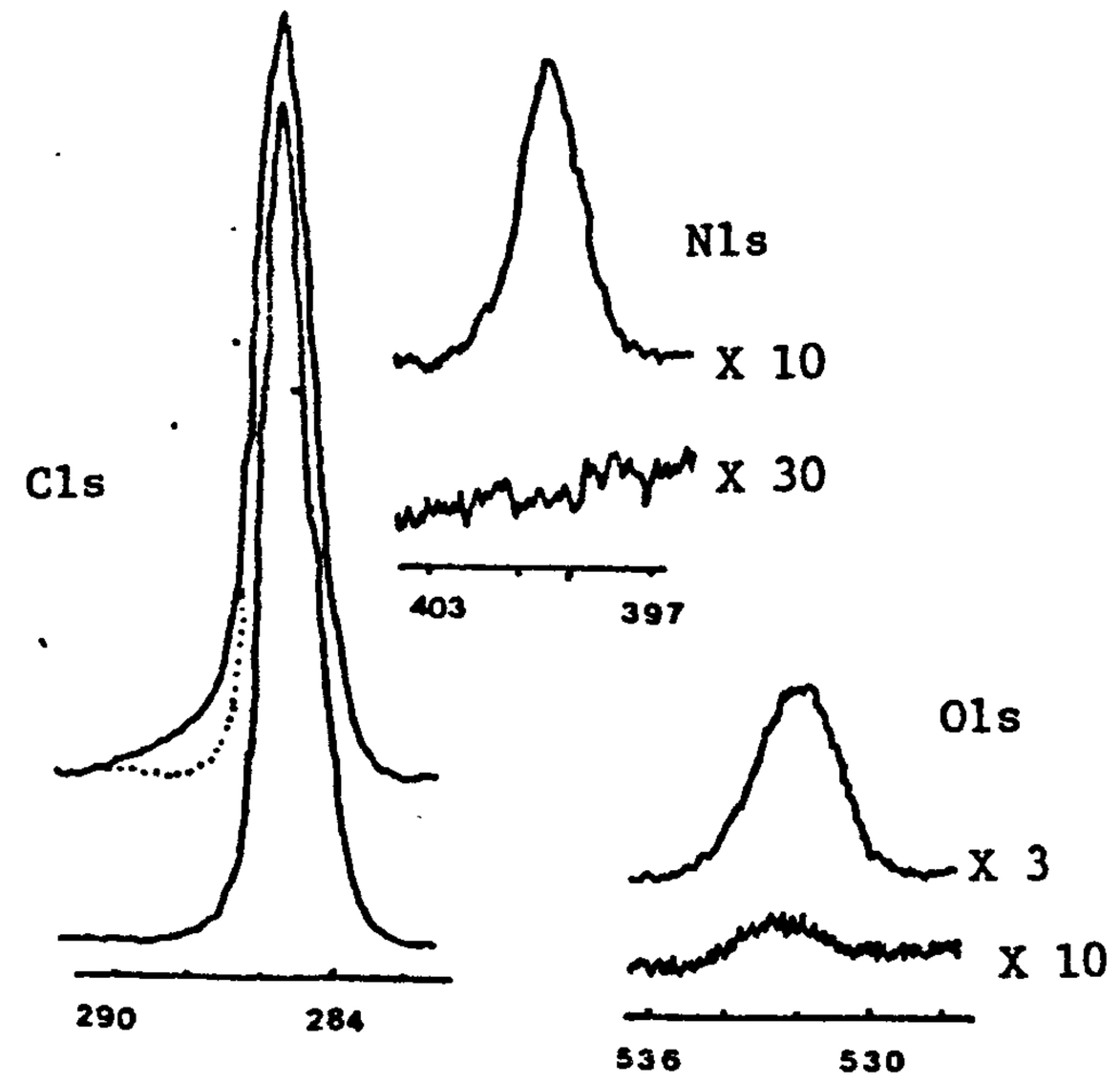
XPS data, and joint strengths for polyethylene extruded onto aluminium

Extrusion conditions	O:C atomic ratio (%)	N:C atomic ratio (%)	Mean Lap Shear Strength MNm^{-2}	Standard Deviation	95% confidence limits	Failure type [a]
Not extruded. Pressed against P.E.T. film. 5 min at 150°C	≤0.6 [b]	0.0	≤0.4	0.03	0.02	I
Extruded at 280°C	7.0	3.0	5.1	0.4	0.3	I & M
Containing 0.02% anti-oxidant. Extruded at 280°C.	0.17	0.46	0.6	0.04	0.03	I
Containing 0.2% anti-oxidant. Extruded at 280°C.	0.0	0.0	0	0	0	I
Extruded at 300°C	5.6	1.5	5.7	0.4	0.3	I & M
Extruded at 300°C with ozone shower	6.8	1.9	6.3	0.5	0.4	I & M
Containing 0.02% anti-oxidant. Extruded at 300°C.	7.4	3.3	4.8	0.3	0.2	I & M
Containing 0.02% anti-oxidant. Extruded at 300°C with ozone shower.	8.4	4.2	5.7	0.4	0.3	I & M
Containing 0.2% anti-oxidant. Extruded at 300°C	1.5	0.43	0	0	0	I
Containing 0.2% anti-oxidant. Extruded at 300°C with ozone shower.	6.2	2.1	3.3	0.2	0.1	I

Notes: (a) I = apparent interfacial failure between polyethylene and aluminium; M = failure of the polyethylene.
(b) Highest figure for film containing 0.2% antioxidant, some of which is probably detected on the surface.

Spectrum 8.

Binding energies of Cls, Nls and Ols peaks from surfaces of untreated film (lower traces) and polyethylene after removal of aluminium foil (upper traces).



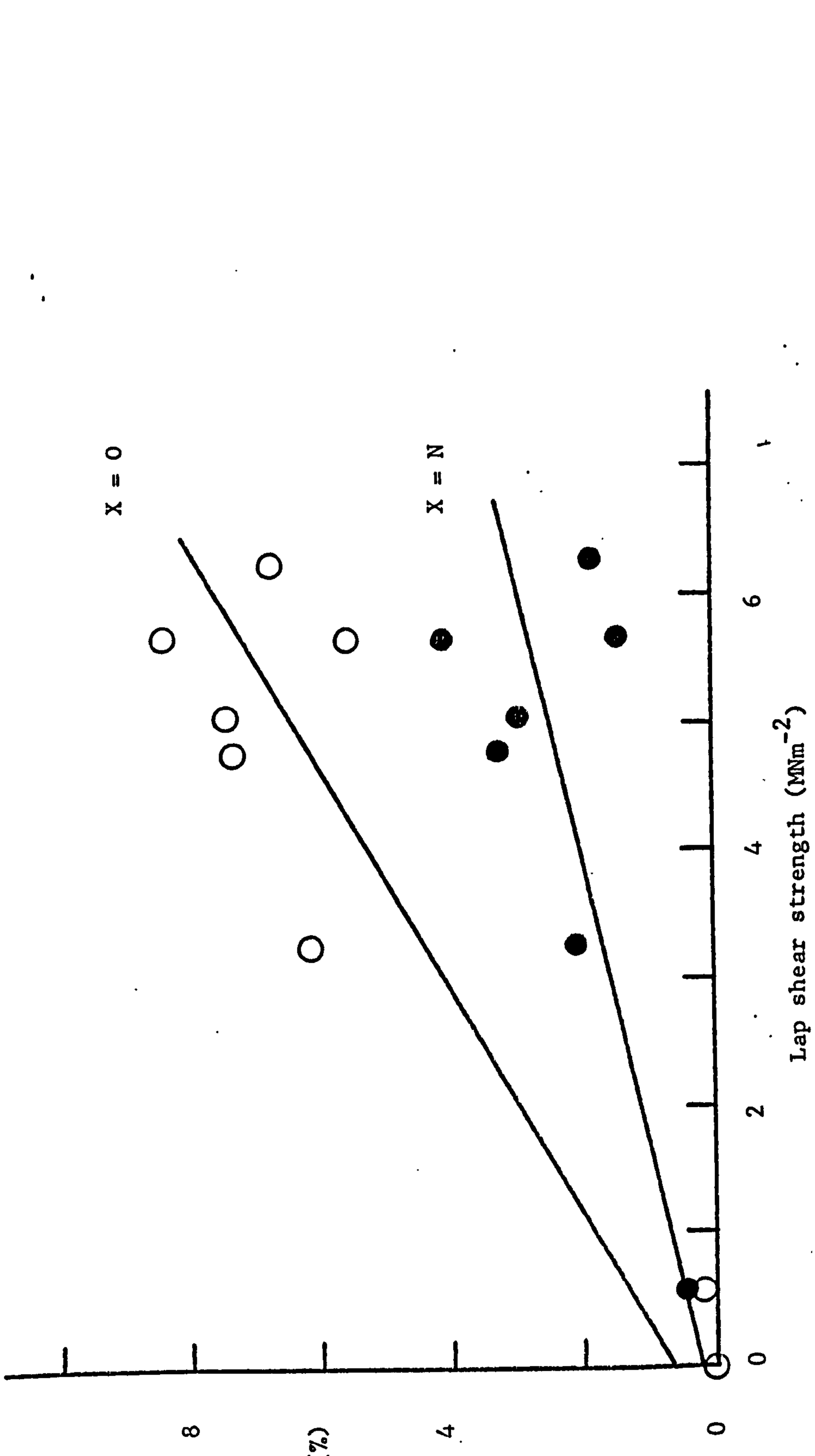

Plot of atomic ratios (%) for O/C and N/C in the polyethylene surface against adhesion level of polyethylene to aluminium in the laminate.
X = O
X = N
X/C (%)
8
4
0
0
2
4
6
Lap shear strength (MNm^{-2})

Fig.26

TABLE 19

Extraction of "Alkathene" WJG47 with a hexane-heptane (5:1) mixture

Details of Treatment	Lap Shear Strengths $MN\ m^{-2}$	Mean	Standard Deviation	95% Confidence limits	Weight Loss	Type of failure
(a) Untreated "Alkathene" WJG47	50 results obtained	0.55	0.03	0.01	-	I
(b) 10 min extraction by mixture	0.55; 0.62; 0.62; 0.66; 0.62; 0.66; 0.76; 0.66; 0.79; 0.62.	0.66	0.07	0.06	0	I
(c) 48h extraction by mixture	0.45; 0.55; 0.52; 0.52; 0.62; 0.60; 0.62; 0.60; 0.52; 0.52.	0.56	0.06	0.05	5%	I
(d) 72h extraction by mixture	0.79; 0.90; 0.79; 0.66; 0.90; 0.81; 0.59; 0.86; 0.81; 1.06.	0.82	0.13	0.1	6%	I
(e) 168h extraction by mixture	1.17; 0.97; 1.72; 1.31; 1.24; 1.31; 1.38; 1.24; 1.38; 1.31.	1.31	1.19	0.2	6.5%	I
(f) 192h extraction by mixture	Environmental stress cracking occurred in the polythene, making it impossible to use the samples	-	-		-	-

Notes: (1) All these samples were vacuum dried for 2 hours at 80°C.

TABLE 20

Extraction of "Alkathene" WJG47 with n-Hexane

Details of Treatment	Lap Shear Strengths MN m^{-2}	Mean	Standard Deviation	95% Confidence limits	Weight Loss	Type of failure
(a) None	50 results obtained	0.55	0.03	0.01	--	I
(b) 8h extraction	0.70; 0.74; 0.68; 0.70; 0.71; 0.75; 0.81; 0.74; 0.71; 0.77.	0.73	0.04	0.03	4.9	I
(c) 24h extraction	1.24; 1.38; 1.10; 1.03; 0.97; 1.10; 1.24; 0.97; 1.17; 1.03.	1.12	0.13	0.1	6.0	I
(d) 48h extraction	1.03; 0.69; 1.24; 0.97; 1.17; 0.88; 1.17; 1.10; 0.83; 1.10.	1.02	0.17	0.1	6.1	I
(e) 165h extraction	1.10; 1.24; 1.31; 1.31; 1.38; 1.03; 1.17; 1.17; 1.10; 1.31.	1.21	0.12	0.1	6.5	I
(f) 338h extraction	0.83; 0.77; 1.10; 1.10; 0.75; 1.17; 0.81; 0.74; 1.17; 1.10.	0.95	0.19	0.2	6.9	I
(g) 676h extraction	0.83; 0.97; 1.03; 0.83; 1.17; 1.38; 0.97; 1.00.	1.02	0.18	0.2	7.7	I
(h) 720h extraction	Environmental stress cracking occurred in the polyethylene making bond strength determinations impossible.				--	--

Notes: All samples vacuum dried at 70°C for 2 hours.

TABLE 21

Effect of ageing on bond strength of hexane extracted "Alkathene" WJG47

Details of Treatment	Lap Shear Strengths $MN\ m^{-2}$	Mean	Standard Deviation	95% Confidence limits	Type of failure
(a) 24h extraction vacuum dried for 2h at 70°C	1.24; 1.38; 1.10; 1.03; 0.97; 1.10; 1.24; 0.97; 1.17; 1.03.	1.12	0.13	0.1	I
(b) as (a) but aged for 7d	0.54; 0.58; 0.55; 0.54	0.55	0.02	0.03	I
(c) repeat of (b)	1.10; 1.17; 1.14; 1.17; 1.03; 1.31.	1.15	0.09	01	I
(d) as (a) but aged 28d	1.21; 1.17; 1.03; 0.97; 1.03; 1.24.	1.10	0.11	0.1	I

Fig.27
Talysurf profile of hexane extracted"Alkathene" WJG47.

Notes: (1) Horizontal magnification = 100X
Vertical magnification = 10,000X
(2) Curve (a) is for untreated "Alkathene" WJG47.
(b) Curve (b) is for hexane extracted "Alkathene" WJG47 (time of extraction = 24h).

TABLE 22

Effect of Trichloroethylene on "Alkathene" WJG47 and "Propathene" HF20

Details of Treatment	Lap Shear Strengths MN m^{-2}	Mean	Standard Deviation	95% Confidence limits	Type of failure
(a) "Alkathene" WJG47 untreated	50 results recorded	0.55	0.03	0.01	I
(b) as (a) but 60 sec in trichloroethylene at 40°C	0.55; 0.45; 0.52; 0.62; 0.62; 0.59; 0.52; 0.59; 0.41; 0.48.	0.54	0.07	0.05	I
(c) "Propathene" HF20 untreated	0.25; 0.26; 0.25; 0.24; 0.25; 0.23; 0.25; 0.26; 0.26; 0.25.	0.25	0.01	0.008	I
(d) as (c) but 5 sec in trichloroethylene vapour	1.10; 1.10; 0.90; 0.97; 1.03; 0.97; 1.03; 0.83; 1.03; 1.03.	1.00	0.08	0.06	I

Notes: All samples vacuum dried for 1h at 70°C.

TABLE 23

Ammonium Persulphate and Peroxide Treatment of "Alkathene" WJG47

Details of Treatment	Lap Shear Strengths $MN\ m^{-2}$	Mean	Standard Deviation	95% Confidence limits	Contact angle θ^{o} adv	Type of Failure
1h in 0.26M ammonium persulphate at 60°C	6.89; 7.24; 7.45; 6.83; 7.24; 7.58; 7.72; 6.96; 7.93; 7.58.	7.34	0.37	0.3	58	M
5 sec in peroxide then 12h at 80°C(a)	0.76; 0.69; 0.69; 0.66; 0.69; 0.66; 0.62; 0.72; 0.62; 0.66.	0.68	0.049	0.03	95	I
5 sec in peroxide then 36h at 90°C(b)	0.83; 9.00; 9.00; 1.03; 0.96; 1.03; 0.83; 1.10; 0.96; 0.90.	0.94	0.089	0.06	93	I
5 sec in peroxide then 5h at 95°C	Samples found to have melted					

Notes: (a) Bond strength of untreated polythene kept in oven for the same time was 0.44 MNm^{-2}

(b) Bond strength of untreated polythene kept in oven for the same time was 0.28 MNm^{-2}

TABLE 24

Use of "Alkathene" WJG47 as the adhesive

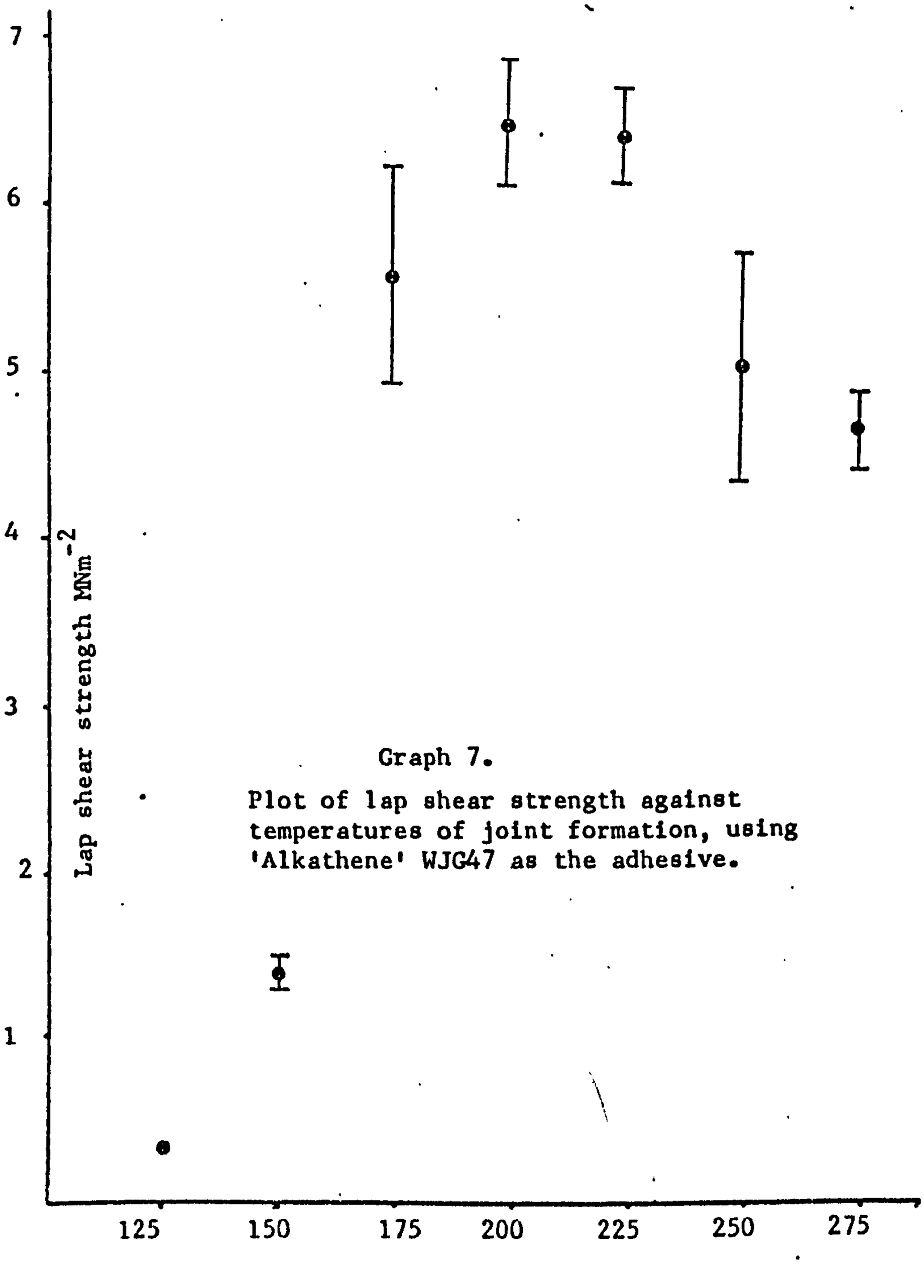
Details of Treatment	Lap Shear Strengths $MN\ m^{-2}$	Mean	Standard Deviation	95% Confidence limits	Type of failure
(a) 5 min at 125°C with pressure of 0.77 $Kg\ cm^{-2}$	0.34; 0.34; 0.33; 0.35; 0.36	0.34	0.01	0.01	I
(b) as (a) but temperature 150°C	1.59; 1.38; 1.31; 1.38; 1.45.	1.42	0.11	0.1	I&M
(c) As (a) but temperature 175°C	4.90; 4.62; 4.96; 4.48; 5.79.	4.95	0.51	0.6	M
(d) As (a) but temperature 200°C	6.21; 6.89; 6.21; 6.89; 6.55.	6.55	0.34	0.4	M
(e) As (a) but temperature 225°C	6.76; 6.21; 6.62; 6.21; 6.62.	6.48	0.26	0.3	M
(f) As (a) but temperature 250°C	5.24; 4.96; 5.38; 4.14; 5.65.	5.07	0.58	0.7	M
(g) As (a) but temperature 275°C	4.83; 4.76; 4.69; 4.83; 4.55.	4.73	0.12	0.2	M +

+ Polythene became yellow and brittle.

TABLE 25

Effect of "Dwell" time on joint strength at 160°C using polythene as the adhesive

Time Min.	WITHOUT SPACERS				WITH SPACERS			
	Mean lap shear strength MNm^{-2}	Standard deviation & sample	95% Confidence limits	Type of failure	Mean lap shear strength MNm^{-2}	Standard deviation	95% Confidence limits	Type of failure
5	0	0	-	I	0	0	-	I
10	1.65	0.12	0.2	I	0	0	-	I
15	5.38	0.46	0.6	I&M	1.86	0.19	0.2	I
20	6.90	0.51	0.6	M	3.17	0.29	0.4	I
25	6.96	0.50	0.6	M	2.62	0.24	0.3	I
30	7.24	0.68	0.8	M	3.32	0.30	0.4	I



Graph 7.

Plot of lap shear strength against temperatures of joint formation, using 'Alkathene' WJG47 as the adhesive.

TABLE 26

Comparison of bond strength of "Alkathene" WJG47 and EVA copolymers

Details of Treatment	Lap Shear Strengths MN m^{-2}	Mean	Standard Deviation	95% Confidence limits	Modulus MN m^{-2}	Type of Failure
(a) Untreated "Alkathene" WJG47	50 results obtained	0.55	0.03	0.01	178 a 159 b	I
(b) Eva 24-03 containing 24% by weight vinylacetate	2.76; 2.76; 3.38; 2.86; 2.62; 2.48; 1.79; 2.69; 2.62; 2.65; 2.21; 2.90; 2.24; 2.55; 2.75.	2.62	0.36	0.20	-	M
(c) Eva A 14271 containing 15% by weight vinylacetate	1.28; 1.70; 1.52; 1.79; 1.52; 1.52; 1.65; 1.86; 1.72; 1.93; 1.31.	1.62	0.210	0.14	36 a 37 b	I

Notes: (a) Values for 1% secant modulus obtained by ICI, Plastics Division, Welwyn.

(b) Values for 1% secant modulus obtained by self.

TABLE 27

Effect of Potential on "Fluon" G163 in contact with a platinum cathode.

Potential (SCE) Volts	Cell Current (mA)	Observations
0.25	0.001	No change
0.50	0.002	"
0.75	0.006	"
1.00	0.030	"
1.25	0.040	"
1.50	0.045	"
1.75	0.050	"
2.00	0.080	"
2.25	0.400	Blackening occurs at point of contact
2.50	3.000	Blackening increases slightly
2.75	7.000	" "
3.00	10.000	" "

Comments:

1. The support electrolyte was used without a source of radical anions.

2. No apparent attack occurred below 2.25 volts. The blackening increases slightly with a further increase in voltage.

TABLE 28

Treatment of "Fluon" C163 with naphthalene anions and by direct contact with electrode (using first cell).

Details of Treatment	Lap shear strength MN m^{-2}	Type of failure	Advancing contact angle in degrees
(a) Untreated polytetrafluoroethylene	0.72	I	112
(b) Polytetrafluoroethylene in contact with lead cathode	2.62	I	-
(c) Electrolysis for 2 hours in unmodified cell. Naphthalene concentration in electrolyte, 0.55% w/v	8.27	M	60
(d) As above but immersed in warm concentrated nitric acid for 5 minutes	7.24	M	58

TABLE 29

Treatment of "Fluon" G163 with Various Radical Anions

USING LEAD CATHODE

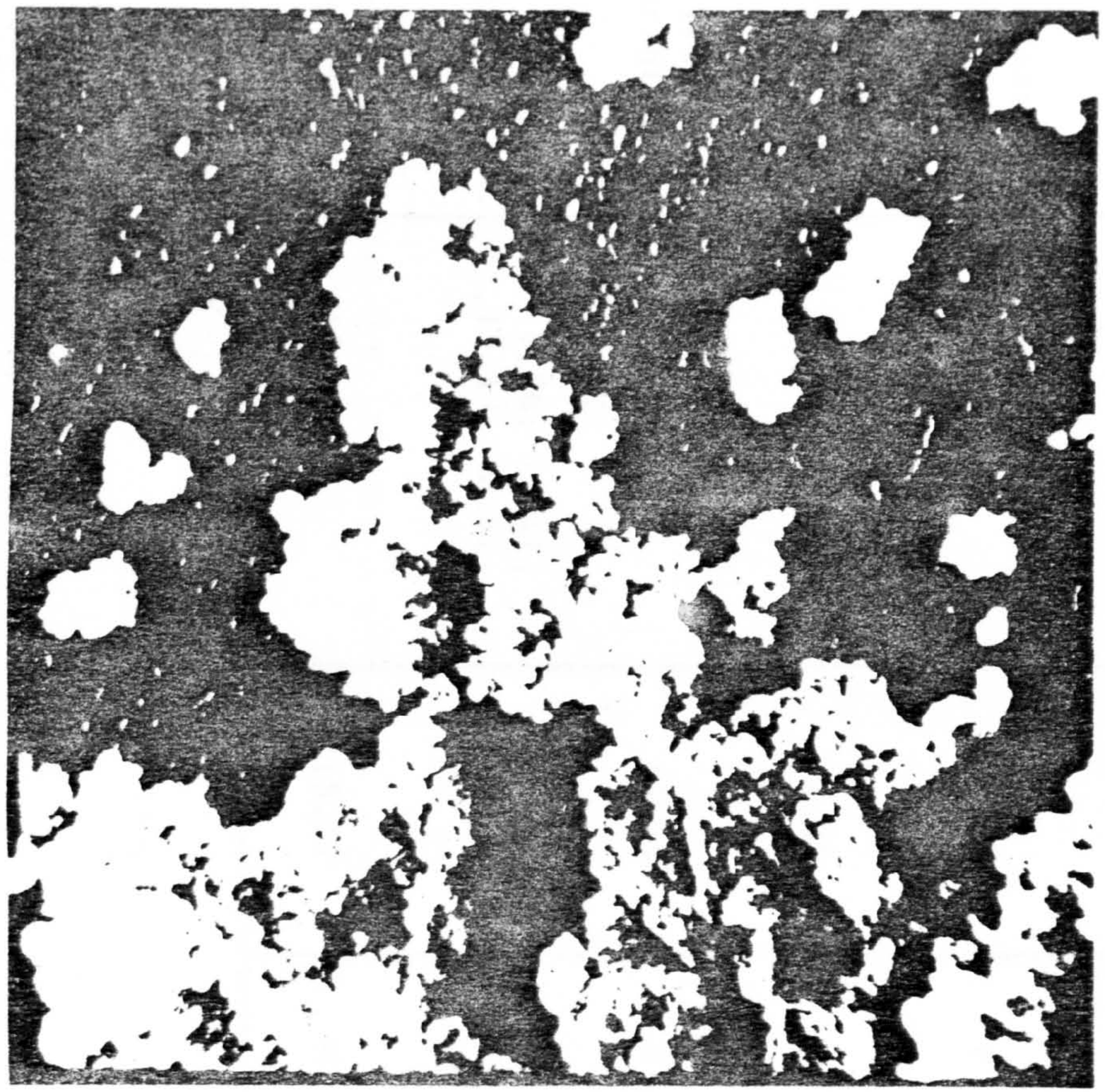
Compound	Potential (SCE) Volts	% Concentration W/V	Time of Electrolysis	Observations
(a) Naphthalene	-2.45	0.55	1 hr	Colour of radical anion-green. Film blackened.
(b) Benzophenone	-1.9	0.55	1 hr	Colour of radical anion-blue no apparent effect on film
(c) Pyrene	-2.025	1.65	1 hr	Colour of radical anion-orange. Film blackened.
(d) Diphenyl	-2.525	1.10	1 hr	Colour of radical anion-dark blue. Film blackened.
(e) Anthracene	-1.98	0.55	1 hr	Not very soluble. Colour of radical anion-blue. No apparent effect on film.
(f) Fluoranthrene	-1.80	1.10	1 hr	Colour of radical anion-orange. No apparent effect on film.

USING PLATINUM CATHODE

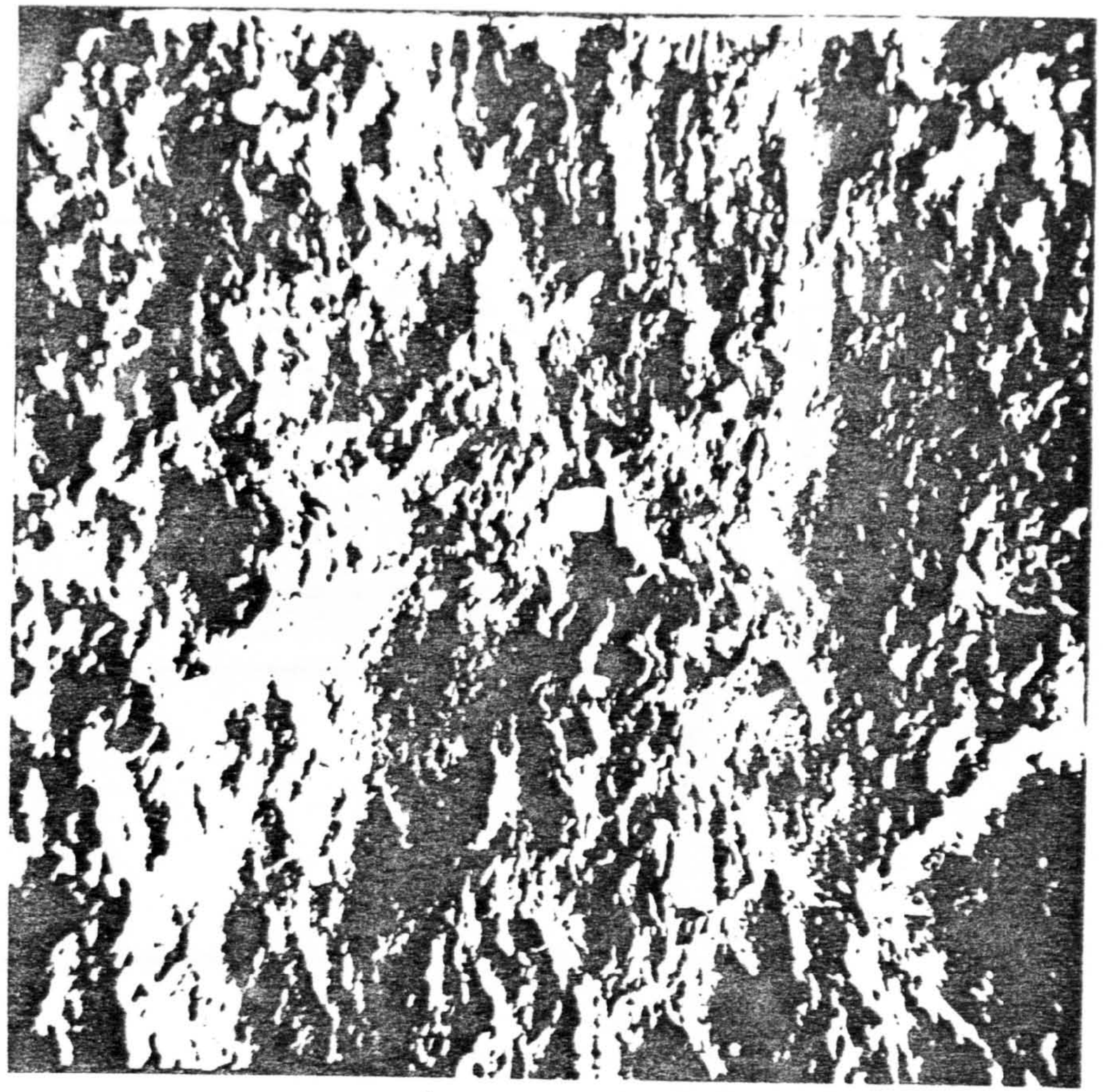
(g) Stilbene	-3.00	2.75	1 hr	Colour of radical anion-orange. Film blackened.

Photo-micrograph 5.

Effect of ageing on treated polytetrafluoroethylene.



a.



b.

a) treated (radical anion attack). Magnification 2100X
b) untreated. Magnification 2100X.

TABLE 30

Treatment of "Fluon" G163 with Naphthalene anions using the Modified Cell.

Type of Treatment	Lap Shear Strengths in $MN\ m^{-2}$		Type of Failure
	Recorded Values	Mean Value	
(a) Untreated Polytetrafluoro-ethylene	.97; .76; .55; .48; .62; .83; .93; .66; .97; .69; .66; .83; .62; .69; .90; .83; .79; .62; .72; .93; .83; .62; .62; .83; .69; 1.07; .66; .52; .69; .69; .90; .66; .72; .66.	0.72	I
(b) 15 min treatment. Ave current 37mA.	2.76	2.76	I
(c) 30 min treatment. Ave current 37mA.	7.14	1.17	M
(d) 45 min treatment. Ave current 6mA.	3.03	3.03	I
(e) 45 min treatment. Ave current 40mA.	10.34	10.34	M
(f) 60 min treatment. Ave current 40mA.	14.75	14.75	M
(g) 90 min treatment. Ave current 40mA.	8.96; 12.41; 15.17; 18.62.	13.79	M
(h) 120 min treatment Ave current 32mA.	15.17	15.17	M

TABLE 31

Treatment of Blackened "Fluon" G163 with Fuming nitric acid

Details of Treatment	Lap Shear Strengths MN m^{-2}	Mean	Standard Deviation	95% Confidence limits	Colour of film after treatment	Type of Failure
(a) 5 min in fuming nitric acid at 80°C	2.62; 2.76; 2.76; 2.83; 2.41.	2.68	0.17	0.2	Yellow	I
(b) As (a) but 15 min treatment time.	2.07; 2.07; 2.14; 2.48; 2.21.	2.19	0.17	0.2	Off-White	I
(c) As (a) but 20 min treatment time.	2.41; 2.34; 2.44; 2.37; 2.41.	2.39	0.04	0.05	Off-White	I
(d) As (a) but 60 min treatment time	1.45; 1.52; 1.24; 1.65; 1.72.	1.52	0.19	0.2	White	I

Notes: (1) The "Fluon" G163 was electrolysed for 90 min to obtain blackening of surface.

TABLE 32

Treatment of Bronze filled "Fluon" VB60 with napthalene anions using modified cell

Details of Treatment	Lap Shear Strengths $MN\ m^{-2}$	Mean	Standard Deviation	95% Confidence limits	Type of failure
(a) Untreated Fluon VB 60	5.52; 6.76; 5.93; 5.52; 5.38	5.82	0.563	0.70	M
(b) 15 min treatment. Naphthalene concentration 0.55% w/w. Average current 38mA	6.55; 6.69; 6.76; 6.14; 6.34.	6.50	0.256	0.32	M
(c) As (b) but treatment time was 30 min. Average current 38mA	6.96; 7.17; 7.03; 6.76; 7.10.	7.00	0.157	0.20	M
(d) As (b) but treatment time was 60 min. Average current 40mA	6.96; 7.58; 7.24; 6.62; 6.83.	7.05	0.374	0.46	M
(e) As (b) but treatment time was 90 min. Average current 38mA	6.76; 6.96; 7.10; 7.24; 6.96.	7.00	0.179	0.22	M

TABLE 33

Treatment of "Fluon" G163 wit' sodium naphthalide

Details of Treatment	Lap Shear Strengths MN m^{-2}	Mean	Standard Deviation	95% Confidence limits	Type of failure
(a) 4 secs in 1:1 mole ratio of sodium naphthalide in THF at 20°C	9.65; 8.96; 8.79; 9.31; 9.65	9.27	0.40	0.5	M
(b) As (a) but 10 secs treatment	10.34;11.03;10.69; 9.65; 9.99	10.34	0.55	0.6	M
(c) As (a) but 60 secs treatment	11.38;11.20;11.03;10.69;11.55	11.17	0.33	0.4	M
(d) As (a) but 180 secs treatment	11.20;10.34; 9.99;11.03;10.69	10.65	0.50	0.6	M

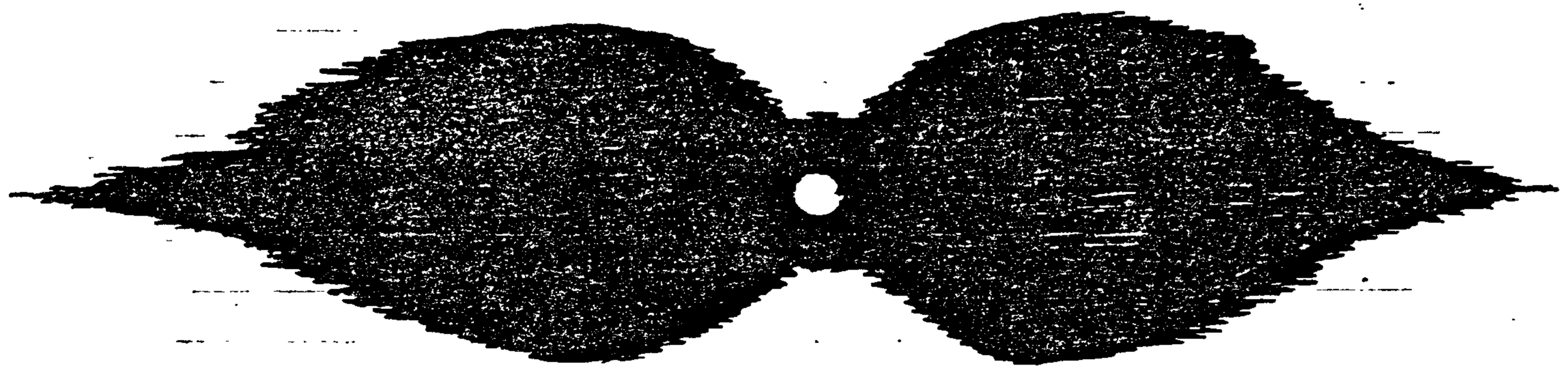


Fig.28
Diagram of the backening obtained on direct contact with electrode.

Note: The fine lines represent skiving marks.

4. Discussion.

4.1 General

The current theories of adhesion are:-

(1) Mechanical;

(2) Electrostatic;

(3) Diffusion;

(4) Adsorption;

(5) Weak Boundary Layer.

Of these, only the last two offer an explanation as to why pretreatments are necessary for successful bonding in polyolefins and polytetrafluoroethylene.

According to the Adsorption theory, polyolefins and polytetrafluoroethylene, due to their chemical nature, have low energy surfaces which are difficult to wet. When an adhesive or ink is spread on such a surface, air bubbles are trapped at the interface between adhesive and adherend. These lead to stress concentrations which enable any bonds formed to be readily broken.

Successful pretreatments alter the chemical nature of the surface by introducing polar groups. Polar groups increase the surface energy of the surface and lead to better wetting by adhesives. This permits good bonds to be obtained.

The Weak Boundary Layer Theory discounts the need for introducing polar groups to improve wetting. Poor bonding characteristics of polyolefins and polytetrafluoroethylene are solely due to these materials possessing inherent weak boundary layers. These are thought to be low molecular weight species. These are present throughout the bulk of the polymer and in the surface. The forces of attraction between this boundary layer and the surface are very weak. The ink or adhesive applied to

the surface, in fact, bonds to this weak layer. However, since the weak boundary layer is weakly held, the ink or adhesive can be removed very easily.

The effect of successful pretreatments is to eliminate the weak boundary layer. This is done by either crosslinking with the bulk or removal by oxidation, etc.

Both these theories have their proponents and there has been much controversy as to which is the better theory. Although many experiments have been carried out, the results are capable of being interpreted either way.

For example, the effect of chromic acid treatment on polyolefins may be considered. It is known that treatment times of about one minute at about $20^{o}C$ are sufficient to produce bondable surfaces in polyethylene. (This is provided the chromic acid composition is approximately $K_2Cr_2O_7 : H_2O : H_2SO_4 = 7:12:150$). ATR studies of polyethylenes thus treated reveal that no apparent change has taken place (83). Similar negative results have been obtained for other commercial levels of pretreatments, such as corona discharge or flame treatment. More severe treatments do begin to show the presence of polar groups.

The adherents of the weak boundary layer theory have offered the following explanation (88). No polar groups are detected at low treatment levels, because there are none to be detected. The treatment has removed the weak boundary layer. While agreeing that more severe treatments show increases in polarity, they point out that this increased polarity does not cause a corresponding increase in bond strength.

Those who favour the adsorption theory have on the other hand maintained that if polarity is present and detectable after severe treatments, it must be present after low intensity treatment. It is not detected

because, either there is not enough to be detected or because instruments used are not sensitive enough.

The two conflicting views were difficult to resolve. Evidence that could prove or disprove either was lacking. No satisfactory proof of the existence of an inherent weak boundary layer was produced. On the other hand, in spite of the implied claims of IR spectrophotometer manufacturers, no machine capable of detecting monolayers was forthcoming till XPS became available to examine at polymeric surfaces (96).

4.2 Discussion of Errors Involved in the Present Work.

All measurements are subject to errors. The size of these depends upon the quality of the measuring devices and the skill of the person concerned. The ideal of having errors so small that these become insignificant is difficult to achieve in adhesion science.

The greatest possible source of error lies in the determination of bond strengths. In this work, the bond strengths were determined as the force required to break a polythene-adhesive bond, determined by means of a Hounsfield Tensometer, "W" type. The results were recorded onto heat sensitive paper and then read off by means of a transparent scale. The manufacturers claim the accuracy of this instrument to be $\pm$2%.

However, the accuracy of the results obtained is also determined by the uniformity (or lack of it) of treatment. This is difficult to assess. A measure of this can be obtained from the scatter of results of the joint strength determinations. In most experiments, a minimum of ten samples was used. This number was decided upon due to limitations of oven space and time available for bonding and testing. (Thirty samples would have been an ideal number). From the results obtained,

the mean was determined. The standard deviation (sample) was found, and using Student's t tables 95% confidence limits of the mean were found. These give a 95% probability that the true mean result will be within those limits. From the results obtained, it can be seen that these limits are about 10% of the mean value. Thus, the error in the joint strength determinations is about 10%. This figure is generally accepted by most workers (89).

4.3 Chromic Acid Etching of Polyolefins.

The effect of chromic acid etching on polyolefins has been the subject of study by several groups of workers (35, 71, 80); the most thorough investigation was that of Blais et al (83), who investigated the topography, wettability and adhesion of etched low and high density polyethylenes and polypropylene. Their surface chemistry investigations were, however, limited to ATR infra red spectroscopy studies, which inevitably suffer from a relatively large sampling depth ($\sim$ 1 μm). Thus in the case of low density polyethylene, long etching times were required (c 1 hour) to obtain spectra which revealed extensive chemical changes. Polypropylene, even after very severe treatment (6 hours) gave unchanged spectra. As a result of their studies, Blais and co-workers concluded that improvements in adhesion could be obtained without the need for oxidation to occur.

The adhesion, wettability and ATR infra red spectroscopic studies of the present investigations into chromic acid etching of polyolefins give very similar results to those of Blais et al. The ATR infra red spectroscopic studies are so similar, that were they not supplemented by XPS data, the conclusions of Blais would have been difficult to avoid. The results of XPS investigations showed for the first time that oxidation of surface occurred even with very mild treatments.

All samples etched with chromic acid gave pronounced O1s, oxygen and S2s and S2p sulphur peaks. Peak areas can be converted into elemental atomic ratios by means of differential cross-sections for core-level excitation. Although values quoted by Wagner (97) were applicable to the spectrophotometer used, internally generated values for C1s, O1s and S2p were used. These were obtained from studies in situ of poly (ethylene terephthalate) and poly(phenylene sulphide). The sharp intensive S2p, sulphur peak had a binding energy of 169.3eV. This, on comparison with the peak for sulphur atoms in poly (phenylene sulphide) when measured under identical conditions, gave a shift of +5.3eV. This is similar to +5.2eV obtained for the chemical shift between R-S-R and $R-SO_2-OR$, by Siegbahn et al (98). From this it appears that $-SO_3H$ groups are introduced into polyolefin surfaces during etching.

If the polyethylene surface was modified only by the introduction of $-SO_3H$ groups, then the O:S atomic ratio would be expected to be 3:1. Table 1 shows that an excess of oxygen is introduced. For polyethylene etched for 30 minutes at 70°C it can be seen that some 1.25% of the carbon atoms are attached to $-SO_3H$ groups. Assuming the remaining oxygen to be combined with the carbon in a 1:1 ratio (as in C-OH or C=O) then there should be 11.5% of carbon atoms involved. Thus a total of 13% of the carbon atoms in the surface should be chemically shifted out of the main C1s peak due to their higher binding energies. Published data for shifts relative to C1s (hydrocarbon) give 3eV for >C=O, 1.5eV for C-OH and 4.5eV for -COOH (99). If the core level spectrum of polyethylene treated for 30 minutes at 70°C (spectrum 1) is examined, a tail on the high binding energy side of the C1s peak can be observed. For untreated polyethylene this C1s peak is highly symmetrical. Deconvolution shows that the high binding energy tail

accounts for about 12% at most of the total C1s intensity. This is slightly lower than the calculated figure. The spread of binding energy out to +4.5eV suggests that there are carboxyl groups present (COOH), which then explains the discrepancy in the result.

In the case of polyethylene treated with chromic acid, the following new peaks were observed by ATR infra red spectroscopy: c3500, c1720, c1630, c1200 and c1050cm^{-1}. The peaks at c.1200 and 1050cm^{-1} also occur when polyethylene is treated with concentrated sulphuric acid. From values quoted in infra red tables (100) these peaks can be assigned as being due to -SO_3H groups. This agrees with XPS results.

Treatment with 2M sodium hydroxide causes the c1730cm^{-1} peak to become the shoulder of a broad peak at c1575cm^{-1} (see fig.16). Treatment with 2M hydrochloric acid causes reversion of the peaks to their original positions. Reactions with ethereal diazomethane, left the c1630cm^{-1} peak unaffected, but the c1720cm^{-1} peak was replaced by a new peak at c1740cm^{-1} (see fig.17). The peak at c1575cm^{-1} is considered to be characteristic of acid salts of carboxylic acids (101) and the peak at c1740cm^{-1} is characteristic of ester carbonyls. Reaction with freshly prepared 2,4-dinitrophenyl hydrazine reagent did not affect the peak at c1720cm^{-1}. The peak at c1630cm^{-1} was replaced by a doublet at 1600cm^{-1}, and new peaks, unaffected by methanol washes were obtained at c1500 and c1300cm^{-1} (see fig.18). These peaks were identical to the peaks of the 2,4-dinitrophenyl hydrazine derivative of acetone.

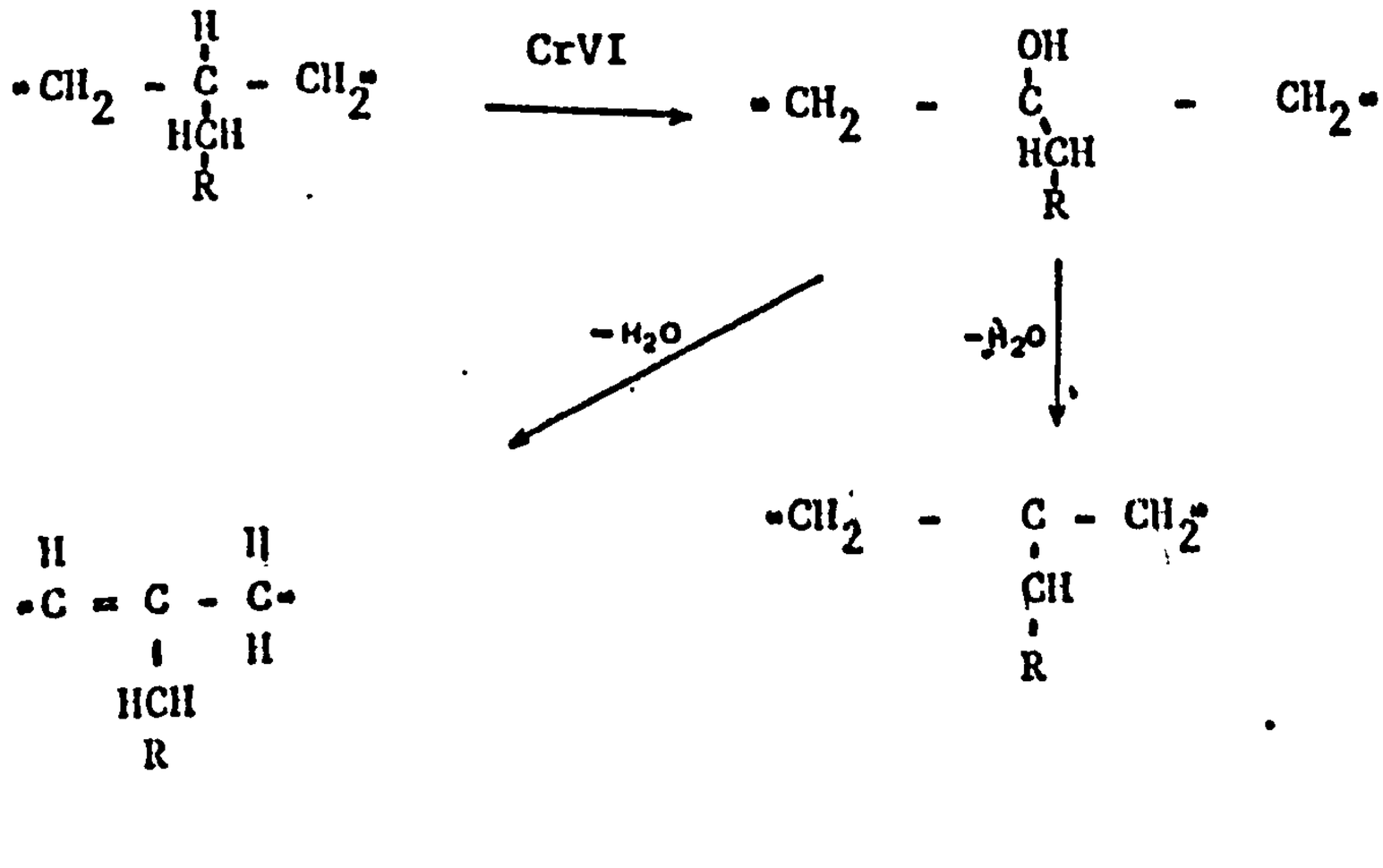
From the above, it can be assumed that the peak at c1720cm^{-1} is due to -COOH groups and that at c1630 to carbonyl (>C=O). Tests were made to see if the carbonyl groups were aldehydic or ketonic, but the results were inconclusive. The other peak that at c3500cm^{-1}, is

characteristic of -OH groups (100). Thus ATR infra red spectroscopy finds the following groups:- OH, >C=O, and -COOH. This is in agreement with XPS determinations.

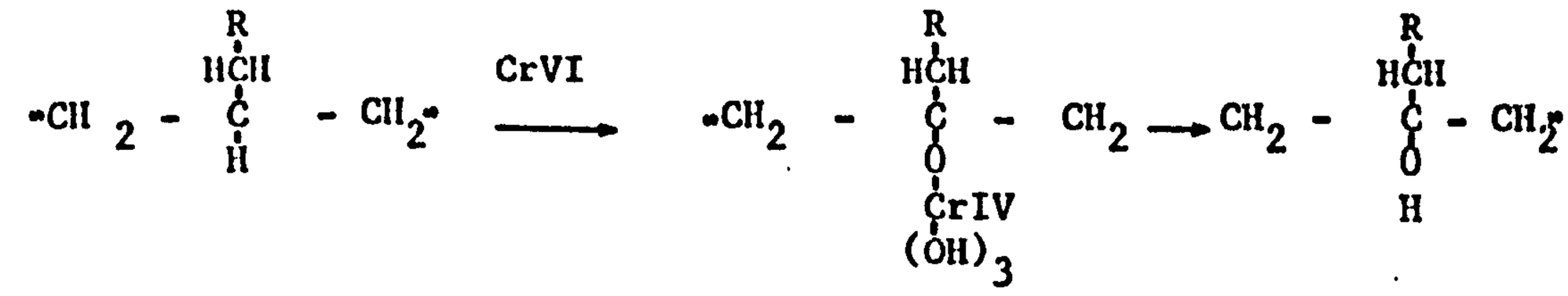
When the potassium dichromate/sulphuric acid system was replaced by chromium trioxide in acetic acid, peaks at c1710 and c1630cm^{-1} were obtained. Increase in treatment time or a four fold increase in chromium trioxide concentration caused the c1710 peak to increase, while the c1630cm^{-1} peak decreased (see fig.19).

Treatment with 2,4-dinitrophenyl hydrazine reagent gave the usual peaks associated with 2,4-dinitrophenyl hydrazones, and the c1710cm^{-1} peak became split into a doublet (see fig.20). Treatment with 2M sodium hydroxide shows some decrease in peak height at c1710cm^{-1} and a new peak formed at c1550cm^{-1} (see fig.21). From this the peak at c1710cm^{-1} appears to be due to both carboxylic and carbonyl groups.

The generally accepted mechanism of attack of polyolefins has been suggested to occur via an alcohol to olefin (102).

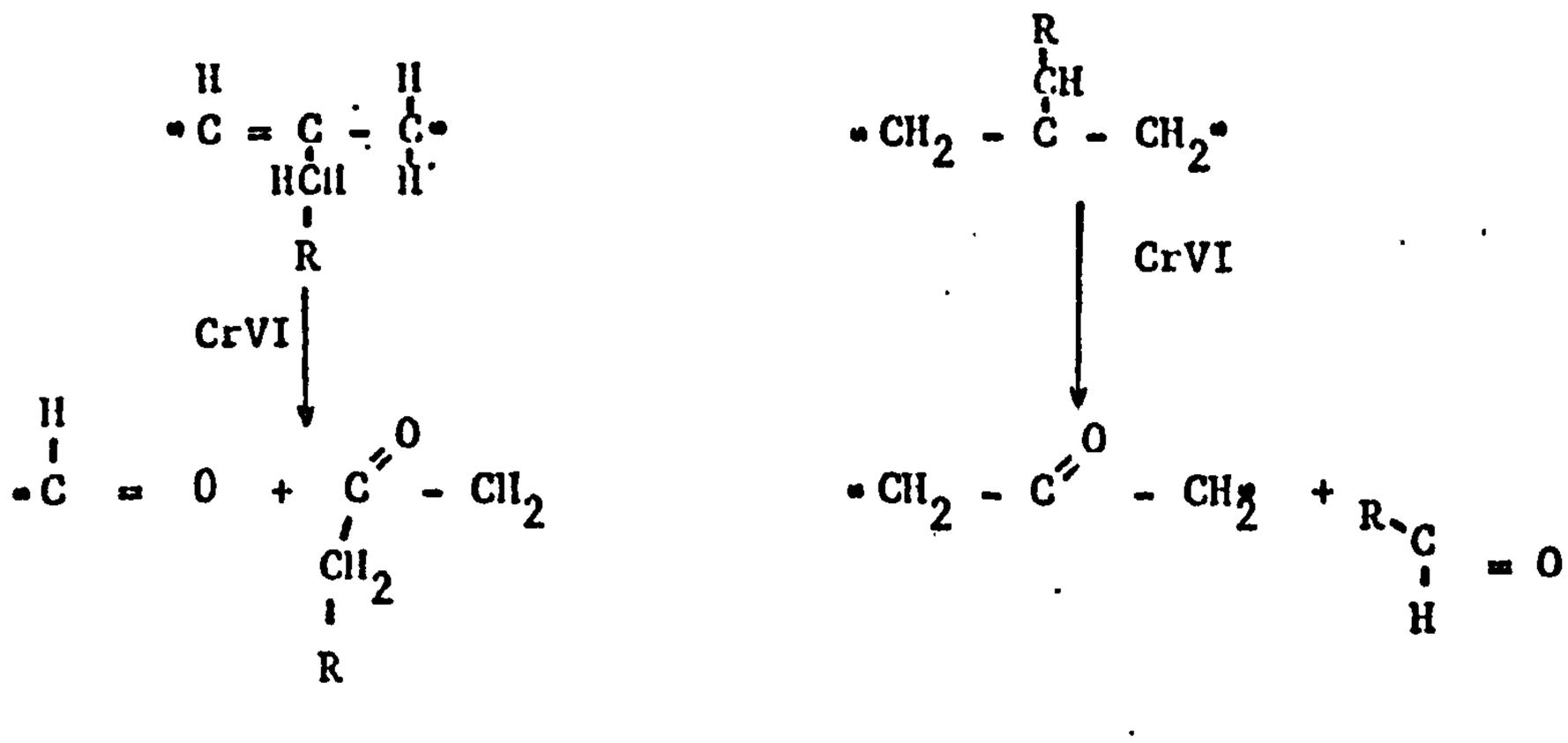


Blais et al have suggested following Weiberg and Eisenthal (103) that the initial alcohol formation is via a chromium IV ester intermediate:



This seems unlikely since no evidence of chromium was found in the mildly treated polyolefins and since treatment with concentrated sulphuric acid also gives rise to oxygen containing groups.

From the olefin stage attack proceeds to aldehyde and ketone, thus:-



The aldehydes and ketones could then be oxidised further to carboxylic acid groups.

The likely site for attack would be the tertiary hydrogen atom present at branch points. As polypropylene has by far the greatest number of those, it is the most reactive and is etched away far more quickly than the low density polyethylene. There is also more likelihood of radical formation and chain scission by means of an "unzipping" mechanism in the polypropylene, which explains why only such a low depth of treatment is obtained.

Valence band spectra of polypropylene and polyethylene, before and after chromic acid etching are shown in spectra 2 and 3. The study of polymer valence band structures by XPS is relatively new, relying on quantum mechanical calculations for interpretation. Most of the published data relates to fluorinated homopolymers (104). However, the valence band spectrum of polyethylene has been reported and assigned (105).

In the spectrum of untreated polyethylene, the doublet in the region of 1226-1238eV is assigned to carbon - carbon bonds (C-C) and the band between 1238-1248eV is assigned to carbon-hydrogen bonds (C-H) (105).

The polypropylene spectrum has not been studied previously, but must contain similar bands. The new peak at 1233eV must be due to the carbon to methyl group bond ($C-CH_3$).

Incorporation of oxygen into the polymer surfaces is reflected by the growth of a new band at c1222eV. This is due to electrons in orbitals with strong 02s character. In the case of polyethylene there is increased growth on this band as etching progresses. For polypropylene on the other hand, there is little growth of this band.

The escape depth in solids increases in a roughly linear fashion from 0.5 to 2 nm with an increase in the kinetic energy of electrons when using Mg Ka radiation from 100 to 1250eV. Thus a high kinetic energy core level will sample a greater depth than a low kinetic energy core level.

The escape depth, λ, is best defined by the integrated intensity equation $Id = Ioo\ (1-e^{-d/\lambda})$, where Id is the elastic peak intensity from a layer of thickness d and Ioo is the intensity from an infinitely thick layer from an electron with an associated escape depth λ. Thus 95% of

the elastic peak intensity originates from a layer 3 Å thick and this can be taken as a useful guide to the depth of a solid actually sampled by XPS. In organic systems the escape depth is now believed to be about 1nm.

In the samples examined the O2s level in the valence band region is semi-core like with a kinetic energy of 1222eV, and samples a greater depth than the O1s level (with a kinetic energy of 717eV). As the depth of polymer that has been etched increases, the O1s:O2s intensity ratio should decrease to a limiting value when the depth reaches ≈ 3 Å (O2s). Although amorphous areas are likely to be etched more quickly than the crystalline, the O1s to O2s ratio can be taken as an approximate guide to the relative degree of attack with the top 3 nm of the polymer. From the O1s:O2s peak ratio data the limiting ratio for the spectrometer used appears to be 9. Table 3 shows that 1 minute at 20°C etches polyethylene almost down to the sampling depth. Polypropylene etched for 6 hours at 70°C is modified to a similar extent. However, 1 minute at 20°C etches polypropylene down to a fraction of this depth. There is very good agreement between these results and those of angular rotation experiments (Table 2). This is confirmation also from the valence band spectra. The results from Tables 1 and 2 show that XPS with a low sampling depth, as compared to ATR infra red spectroscopy, is a much more sensitive technique for studying chemical changes in surfaces. For samples with a depth of modification greater than ≈ 1 μm it is in agreement with ATR spectroscopy. For samples that have not been modified to this depth, it is the only technique capable of monitoring surface chemistry changes. It shows that polypropylene is oxidised by chromic acid. It also shows that the depth of modification is not large. This is why those who studied chromic acid etching of polypropylene

using ATR infra red spectroscopy could find no evidence of oxidation. XPS has also shown that mild chromic acid treatments (1 minute at 20°C) introduces substantial oxidation. This is an important new finding in adhesion science, since it offers definite proof that oxidation can occur with mild chromic acid treatments. This work has since been published (106).

It is interesting to see that Table 6 shows that oxidation is induced by even milder chromic acid treatments. Decreasing the dichromate concentration to 1% normal still leads to an appreciable increase in the oxidation of polyolefin surfaces. This increase in oxidation level is accompanied by an increase in joint strength. Removing the dichromate - leaving only concentrated sulphuric acid - leads to a substantial decrease in both oxidation level and joint strength. It requires an increase in the severity of treatment (1 hour at 70°C) to give moderate adhesion and oxidation levels. Even then, these are not restored to the level obtained when 1% normal dichromate is present.

It can be seen, especially with concentrated sulphuric acid, that an increase in the presence of SO_3H groups does not appear to cause a corresponding increase in adhesion. It thus looks that SO_3H groups do not appear to contribute to increased adhesion. This is in contrast to carbon-oxygen species, where an increase in the level of these leads to increased adhesion. This suggests that SO_3H groups do not play an important role in adhesion to epoxy adhesives.

Overnight washing of etched samples shows a decrease in oxidation levels, when compared to a normal wash. This suggests that certain relatively low molecular weight species are left on the treated film surface. These take no part in adhesion but increase the oxidation level. It was found that wiping with an acetone soaked tissue removed some of the

oxygen and sulphur containing species. Other evidence for this is provided by Rasmussen et al (107), who showed that carbonyl group levels are decreased by extracting chromic acid etched polyethylene with 2-propanol. However, an extensively oxidised surface is still left, and this is not affected by further washing or extraction.

As they found no evidence of oxidation after etching of polypropylene, Blais et al claimed that this was compelling support for the weak boundary layer theory. XPS results, however, show that there is substantial oxidation even for the mildest chromic acid treatment. Comparison of O1s to O2s values shows that there is a difference in the depth of modification of polypropylene surface. Only in the case of severe treatment is the depth of etching greater than sampling depth. Even, then this depth of treatment is too shallow to be detected by ATR.

The more severe treatment of polypropylene gave higher contact angles than the mild treatment. This is in agreement with the findings of Blais and co-workers. However, they suggested that severe treatment caused less oxidation than the mild. XPS results show that the degree of oxidation is about the same. Scanning electron microscopy shows that there is considerable roughening of the surface, which Blais et al did not find. Others (80) however have also found roughening of the polypropylene surface to occur with the chromic acid. The effect of surface roughness has been discussed elsewhere (108) and would certainly increase the contact angle. Further evidence for surface roughness comes from the 6 hour etching of polyethylene when the acid was not changed. The film thus obtained showed a white and green striated surface. It gave a contact angle of 105^{o} and a very rough surface profile when examined by means of the talysurf.

Attempts at "reducing" the surface of chromic acid etched film were not successful. This is due to the fact that only ATR infra red spectroscopy could be used to follow the reaction sequence. There is little doubt that the chromic acid treatment was too severe for subsequent "reduction" reactions. As ATR techniques were employed a thick enough layer had to be formed to be detected. In view of the high bond strength and low contact angle, the "reduced" surface must still have an oxidised layer on it. In future work of this kind, XPS techniques must be employed. This will allow much shorter etching times. Also because of the greater sensitivity of XPS, there will be more certainty as to whether the "reduced" surface is in fact reduced.

Extraction of the treated surface of polyethylene left brown needle-like residues. These could not be dissolved further even by changing to other solvents. Blais and co-workers reported that their residues dissolved in aqueous ethanol and were probably highly oxidised species, rather than cross-linked material. The residues found during this work, did not dissolve appreciably in aqueous ethanol or other solvents, see Table 5. On grinding down with KBr powder they showed extensive oxidation, so they are oxidised species, but the extraction experiments indicate cross-linking.

4.4 Flame Treatment.

XPS investigations of untreated samples showed very low levels of oxidation. Flame treated samples showed strong O1s peaks and sometimes weaker N1s peaks. Peak areas were converted into relative atomic concentrations, using relative elemental sensitivity factors determined for pure organic materials sublimed in situ, using the same spectrophotometer. These factors are O:C-1.55 and N:C-1.30.

Spectrum 4 shows a typical polyethylene surface before and after flame treatment. Deconvolution of the C1s peak for the most oxidised surface, shows three peaks of higher binding energy than the untreated hydrocarbon C1s peak. (In spectrum 4 these peaks are shown by dotted lines). As discussed in the previous section, these can be identified as carbon singly bound to oxygen such as C-OH, C-O-C, and ►C=O for the lower increase in binding energy, and carbon doubly bound to oxygen such as COOH and COOR for the higher (~4.5eV) increase in binding energy. The broad O1s peak at c532eV does not shed further light, since all the oxygen functions have binding energies near 532eV. The exception is the carboxylic oxygen (O-C=O) which has a higher binding by 1.5eV and can be seen in the "tail". The N1s peak is also broad and is asymetric on the high binding energy side. The main contributor to this peak has a binding energy of 399.8eV. This is consistent with the presence of $-NH_2$ or CN groups (99). The minor contributor has a binding energy too low to be assigned to directly oxidised nitrogen groups such as NO_2. It is, however, consistent with $-\overset{O}{\overset{\|}{C}}-NH_2$ or $-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-$ groups.

Valence band spectra (spectrum 5) of flame treated polythene are similar to those of chromic acid etched polyethylene (see spectrum 3). The O1s:O2s ratio which can be used to assess the depth of treatment, is in all cases greater than the value of ~10, obtained for homogenous samples. The values obtained range from 16-20 and follow a trend which increases as the overall level of oxidation decreases.

Angular variation spectra were also obtained for the least oxidised polyethylene sample. The difference between the O1s:O1s intensity ratio for electron take-off samples of 10^{o} and 75^{o} (the angles are with respect to the surface), was within experimental error.

The depth of treatment can be assessed from both the angular variation data and the O1s to O2s intensity ratios. This assessment depends on the knowledge of inelastic electron mean free paths in polymeric materials. From the discussions of Clark and Thomas on this subject (109) it can be assumed that λ C1s = 1.4nm and λ O2s = 3nm. If O1s:O2s ratios were greater than ~ 10 it would suggest that oxygen is unevenly distributed within the O2s sampling depth (ie 3 λ (O2s) ~ 9nm). However, lack of angular dependance of the O1s:C1s ratio, implies homogenity within the C1s sampling depth (3 λ (C1s) ~ 4.2nm). This then suggests that the treatment depth, d, must lie between 4.2 and 9nm (ie $4.2nm < d < 9nm$).

Although there has been work done on the effect of flame treatment (110), there has been no evidence available to support the views put forward. The above findings show that the oxidation of the surface is limited to a layer thinner than 9nm. This thickness is too thin to be detected by ATR infra red techniques, and explains why this layer has not been detected till now.

The combustion of hydrocarbons, such as natural gas, is a complex process (111). There are many excited species likely to be present in the flame. These will include free radicals, ions, atoms and electrons. In view of the fact that marked variations in surface chemistry, especially the number of nitrogen groups (Table 8) occur, when the gas composition is altered, it appears that these species do not take part directly in the surface modification process. The possible species are likely to be excited states of O,NO,OH,NH and CN. There is every possibility that radicals are produced in polymer chains by ionization events. These radicals will react with oxygen by well recognised

mechanisms to produce the C-OH, C=O and COOH groups found to be present by XPS.

The degree of oxidation of low density polyethylene with the "normal" flame treatment was similar to that found with polyethylene after a severe chromic acid treatment (Table 1). There is a high degree of correlation between the degree of oxidation (as measured by XPS) and adhesion levels. This holds for both additive free and antioxidant containing polymer. This correlation must be treated with a certain amount of caution, since the adhesion levels are similar. There is also the fact that the effects of milder treatments could not be investigated. On the other hand, it can be seen from the results that varying the treatment parameters (such as gas to air ratios) does bring about distinct changes in surface chemistry. This is especially evident in the proportion of nitrogen functions. Whether the nitrogen functions play a part in adhesion, is uncertain, although there is a degree of correlation between the number of nitrogen containing species and adhesion. Further investigations into this are required. However, it appears that oxidation and adhesion levels are related. From this it can be predicted that poor adhesion after flame treatment will be found to be associated with low levels of oxidation.

It is possible that the high oxidation values in Table 8 are due to so called "over-treatment". This occurs when films are oxidised more than is necessary for adequate bonding, and low molecular weight oxidised species are left on the surface. As flame treatment is a "dry"process, compared to chromic acid etching, these oxidised debris are not removed by washing. As was shown in the previous section, even after chromic acid etching and subsequent washing, some oxidised material can be still removed from the surface by wiping with an

acetone soaked tissue. It is fairly certain that a similar situation could occur in the present case.

The effect of having oxidised debris present is probably more important in printing operations rather than in bonding with long-curing epoxy adhesives. These debris are probably displaced by the adhesive during bonding and so strong bonds are formed. In the case of printing, drying times are very fast and solvents are unlikely to penetrate the debris layer. It has been reported that print will peel off in such cases, when the films are stored in moist conditions. Presumably, the debris are hydrophilic and readily absorb water which forms a layer between the true surface and the ink.

The data in Table 8 shows that antioxidant used at the 200ppm level has little effect on the surface chemistry changes after flame treatment, under the conditions employed. It is well known that antioxidants impart an induction period to the polymer they protect (112). The length of this induction period depends on factors such as temperatures and concentration of oxidising species. In this case, antioxidant affords little protection. It is either removed from the surface by vaporisation, or the treatment conditions are severe enough to reduce the induction time to almost zero. The polyethylene films were about 5mm away from the tip of the inner cone of the flame during treatment. Although it was not possible to measure the temperature, it is accepted that this is the hottest region of the flame. Temperatures of the order of 2000°K have been reported for this region (113).

Results of the effect of long term ageing also support the contention that flame treated polyethylene does not suffer serious deterioration in adhesion levels, if adequately protected (114). XPS results show little change in the surface after ageing, and are supported by the lack of

significant deterioration in adhesion levels as shown in Tables 9-11.

4.5 Corona Discharge Treatment.

The effect of corona and related discharge treatments in various gases has been the subject of much study (16, 115, 116). Schonhorn's CASING is only a modified form of corona discharge (18). The majority of authors used ATR infra red spectroscopic techniques to examine the treated surfaces. More recently (91) XPS has been made use of for surface examinations. In the present study, the effects of commercial levels of treatment in air were examined by means of joint strengths, ATR infra red spectroscopy and XPS. The ATR infra red spectroscopic techniques revealed no changes in surface chemistry. This in view of the relative thick depth of modification required, as shown in the preceding two sections, is hardly surprising. With the most sophisticated equipment and techniques, Blythe et al (91) required treatment times of 4 seconds in air to obtain ATR results indicating surface oxidation.

The very limited XPS studies carried out in this work reveal that surface oxidation has occurred. In Table 12 they are shown as O:C% atomic ratios. As they were obtained in the same way (same machine parameters) they can be compared with other experimental XPS data quoted in this work. The data in Table 13 are in the form of peak heights ratios. These were obtained under different machine parameters and cannot be used for direct comparison. They do, however, show that substantial oxidation has occurred.

If the XPS results in Table 12 are considered, this shows that oxygen and nitrogen functions have been introduced. While it can be seen that oxidation has occurred to a similar extent in polyethylene with

and without antioxidant and in polypropylene, the adhesion levels of polypropylene are much lower than that of the two polyethylenes.

Table 13 shows similar results. Adhesion and oxidation levels of treated polyethylenes with and without antioxidant are similar. The adhesion of polypropylene is considerably lower. This difference in adhesion levels for polypropylene and polyethylene is at first surprising. Comparison with chromic acid treatment shows that very high adhesion levels can be obtained with polypropylene, for relatively low levels of oxidation.

The answer lies in the mechanism of attack. It is generally agreed that corona discharge processes are of a free radical type (117). A variety of possible radical species among them the various oxygen and nitrogen fuctions have been proposed (118). Thus, the presence of oxygen and nitrogen containing groups in the surface of the treated polymers can be explained. A radical mechanism does also lead to unsaturation. This can then lead to either cross-linking or degradation by an unzipping type mechanism. In the case of polypropylene with its availability of tertiary hydrogen atoms, degradation is likely to be the main mechanism. The mechanical properties of the polymer will be drastically impaired and adhesion will decrease. The brittle behaviour of treated polypropylene supports this view. The low molecular weight species produced by the degradation process will be readily oxidised. These will be present in the surface, but take no part in adhesion. In a wet process they could have been removed by washing, but as corona discharge is a dry process, they will remain. XPS work in which the experiments are repeated, but the surface extracted and then re-examined, would prove (or disprove) this assertion.

In the case of polyethylene, free radical mechanisms are more likely to lead to oxidation and cross-linking. There will still be low molecular weight oxidised species on the surface, but there will be far fewer than in the case of polypropylene. A much larger proportion of the true surface is likely to be oxidised. The lack of effect of antioxidant on the oxidation levels can be explained in terms of the severity of the treatment. With the large numbers of oxidising species available, the induction effect of the antioxidant is reduced very rapidly, similarly to the flame treatment. If higher antioxidant loadings were used then a decrease in surface oxidation and adhesion levels would occur.

The adhesion values in Table 13 show a negative correlation between power output and adhesion levels. The Table also shows that higher haul off speeds are correlated with higher adhesion levels. This appears contrary to expectations. As mild treatment leads to high adhesion and high oxidation levels, higher values would be expected with more severe conditions. As this is not so, there is a strong possibility that over-treatment has occurred. With the most severe treatment it would seem probable that severe overtreatment has occurred. This has led to the formation of a relatively thick debris layer. A layer so thick that it inhibits adhesive penetration. Unfortunately, there is a lack of XPS data for these samples. Certainly future work should endeavour to investigate this occurrence.

There has been much disagreement in the processing industry about the effect of ageing on adhesion of corona treated polyethylenes. Kim et al (119) report that industrial users find a decrease in printability. Buchel (120) however; found that ageing of up to 6 years had no effect on adhesion values. The adhesion measurements of corona treated

polyethylene in this work show little deterioration with time, and are in agreement with Buchel. The reason could be due to better storage conditions than in industry.

4.6 Nucleation in contact in aluminium.

The aim of this series of experiments was to re-examine the work of Schonhorn and Ryan (19). Schonhorn and Ryan melted polyethylene against aluminium foil and poly(ethylene terephthalate). They found that polyethylene melted againstpoly(ethylene terephthalate) gave poor bond strengths. When polyethylene was melted against aluminium foil, poor bond strengths were obtained if the foil was peeled off. However, if the aluminium foil was dissolved away, good bond strengths with the polyethylene thus obtained, resulted. Schonhorn and Ryan examined the polyethylene surfaces using ATR infra red spectroscopic techniques, and found no evidence of surface oxidation. Schonhorn and Ryan then concluded that oxidation was not necessary to obtain good bonding, and ascribed the increase in adhesion as due to other causes. As the XPS technique was available in the present course of study, it was decided to examine the treated polyethylene surfaces using XPS.

XPS spectra of polyethylene surfaces melted against poly(ethylene terephthalate) revealed relatively clean surfaces. Oxygen species were present in quantities, about 0.25 atomic %. The spectrum of "Alkathene" WJG47 melted against poly(ethylene terephthalate) was identical to the spectra of untreated "Alkathene" WJG47 used in chromic acid and flame treatments. After melting against aluminium the oxygen peak increased considerably. The C1s peak (spectrum 6) shows asymmetry on the high binding energy side, due to the presence of oxidised carbon atoms. From the values obtained, this indicated that C=O groups are formed. Values for O:C atomic ratios are shown in Table 16. These

were calculated from C1s and O1s peak areas corrected for their differing X-ray photoemission cross-sections. These were determined for the instrument using poly(ethylene terephthalate).

Small N1s peaks were observed in the spectra of some of the treated samples. Peaks characteristic of SiO_2 appeared in samples of "Rigidex" melted at 175°C. Since these peaks obscured the O1s peaks, no O:C data have been included in Table 16.

There was no evidence of Al or Na in the spectra of treated samples that had been subjected to 2M sodium hydroxide solution. This indicated that all the aluminium had been removed and sodium hydroxide residues washed off.

In a different experiment, "Rigidex" 50 was again melted against aluminium. This time, one foil was peeled away. The resulting two surfaces were examined by XPS. The O:C ratio of the exposed polyethylene surface was only 0.2%. "Clean" aluminium foil surface revealed the expected oxide on metal spectrum (spectrum 7). However, an intense C1s was also found. This is not surprising, since aluminium foil surfaces are contaminated by a strongly held hydrocarbon layer formed during the rolling process (121). This hydrocarbon layer is not removed by extraction or treatment with chromic acid. The peeled aluminium foil revealed a thicker carbon overlayer. Deconvolution of the C1s peak for this showed evidence of oxidised species. C1s and Al2p peaks of "clean" and peeled foil are shown in spectrum 7. The C1s:Al2p ratio is much higher for the peeled foil. This indicated that the oxidised layer on the polyethylene surface obtained when aluminuim is dissolved off, remains on the aluminium when the foil is peeled away from the polyethylene.

Bromination experiments were carried out on the treated polyethylenes. The results are shown in Table 17. Assuming that bromination only occurs in double bonds, low density polyethylene melted against poly (ethylene terephthalate) gives an unsaturation level of 0.7%. After melting against aluminium foil at 150°C for 10 minutes, this rises to 1.9%. High density polyethlyene ("Rigidex" 50) melted against poly (ethylene terephthalate) gives a value of 0.01%, and when melted against aluminium this rises to 0.9%. These figures must be treated with caution, since crystallinity will affect the bromination process; also there is a possibility of side chain bromination. However, the results do indicate that there is an increase in unsaturation levels.

The presence of SiO_2 peaks in the XPS spectrum of polyethylene melted against aluminium at 175°C was the beginning of a period of problems associated with the use of XPS. Most of the samples supplied for XPS showed this obstructing peak. This problem continued to occur, in spite of trying to avoid obvious sources of SiO_2. It was eventually discovered that only samples coming into contact with distilled water were affected. Various devices, such as steam cleaning all apparatus, redistillation of water, use of deionizing columns were attempted to eliminate the peak. However, the peak was only reduced in size to about one third.

Further investigation showed that the problem occurred just after transfer from one building to another. The distilled water from both buildings (supplied from the same water main) was examined. The water from the "new" building gave rise to the SiO_2 peak.

In subsequent work, distilled water from the "old" building was used, and no more problems were encountered. Although the problem was

resolved, there is no explanation available as to why the SiO_2 peak could occur, even after triple redistillation.

The results from Table 16 show that melting polyethylene against aluminium does produce substantial chemical modification of the polyethylene surface. These findings are borne out by the findings of Clark et al (121) who melted polyethylene against aluminium in order to obtain an oxygen free surface for fluorination. These results are in direct contrast to the conclusions of Schonhorn and Ryan (19) who on finding no evidence of oxidation by ATR spectroscopy decided that no oxidation had taken place. Contact angle determinations, which were also found by Schonhorn and Ryan to show an increase in wettability, also bear out the fact that surface polarity is increased. Schonhorn and Ryan explained this decrease in contact angle as due to changes in surface crystallinity caused by the formation of a Transcrystalline Region. They used the concept of the transcrystalline region to explain the increase in bond strength.

They stated that the weak boundary layer present in polyethylene was entangled up in the long polymer chains during the formation of this transcrystalline region. Removal of this layer by peeling away the aluminium revealed the bulk polymer which contained weak boundary layer material. This peeling effect can be explained as removing the well adhering oxidised surface layer, leaving an untreated, and therefore difficult to bond surface.

There is no doubt about the existence of the transcrystalline region. However, there is evidence that it can be produced on melting against poly(ethylene terephthalate). Fitchmun and Newman (85) found that the transcrystalline surface region is a function of the polymer's thermal history - for a given melting temperature and cooling conditions, the morphology of the polyethylene surface was independent of the substrate

against which it was melted. These workers produced photographic evidence of the transcrystalline region of polyethylene, melted against poly(ethylene terephthalate). They also showed that it was possible to obtain polyethylene melted against aluminium, which did not have a transcrystalline region.

These considerations undermine the weak boundary layer concept. Even if oxidation of the surface is dismissed as purely fortuitous, then why is there a weak boundary layer present on melting against poly(ethylene terephthalate) and not against aluminium? In both cases there is a transcrystalline region, yet in one case there is no increase in bondability and considerable increase in the other. Contact angles show a decrease in the case of the aluminium substrate, but not for poly (ethylene terephthalate). Schonhorn and Ryan claimed that contact angles decreased because of the formation of the transcrystalline region. As both aluminium and poly(ethylene terephthalate) surfaces have been shown to cause the transcrystallinity, similar contact angles could be expected. The results of the present work, as well as those of Schonhorn, show that this is not the case.

There is further supporting evidence of the need for oxidation to occur. Bright and co-workers (89) who have shown that in certain specified cases adhesion of polyethylene to anodised aluminium can be explained in terms of mechanical keying, still show that oxidation of polyethylene is essential when the mechanical keying explanation cannot be invoked. The degree of oxidation is higher in high density polyethylene film than in low density film when moulded under identical conditions. In view of the greater number of reactive sites available in low density polyethylene (tertiary hydrogen atoms at branch points), the opposite would have been predicted. However, experiments with bromination of

the surface (Table 17) shows that low density polyethylene has more double bonds. It is possible that more low molecular weight oxidised species were produced in low density polyethylene, and that these have been removed from the surface during washing with sodium hydroxide and hydrochloric acids. The levels of adhesion are higher for low density polyethylene than for high density polyethylene, despite the low degree of oxidation. No convincing explanation is apparent.

It is interesting to consider the origin of the oxidising species in this treatment of polyethylene. Pressing against aluminium gives higher adhesion values than against poly (ethylene terephthalate) (12-15X) and this is matched with increased oxidation (Table 16). This could be due to either a specific catalytic effect of aluminium/aluminium oxide or due to air being trapped in the relatively rough (as compared to poly-(ethylene terephthalate) aluminium surface. Work by Egorenkov et al (112) shows that alumina has little or no effect on the oxidation of additive free polyethylene. This then is evidence against the possibility of catalytic action. There is, on the other hand, evidence for the trapped air hypothesis in the work of Clark and co-workers (121). They found that in order to obtain oxygen free polyethylene surfaces after melting against aluminium, the polyethylene powder used and presumably the aluminium film had to be degassed several times in argon before bonding under nitrogen. Pressing the polyethylene under nitrogen, without degassing showed oxidation of the surface to have occurred.

The findings discussed here were considered to be of value to others and have been published (122).

4.7 Extrusion coating of polyethylene onto aluminium.

Extrusion of polyethylene onto aluminium foil provides polyethylene-aluminium laminates. These because of their excellent barrier

properties and easy heat sealability are of importance in various packaging applications. The object of this set of experiments was to determine what effect processing conditions would have on adhesion and oxidation levels. A different low density polyethylene, "Alkathene" WNC71 was used. Since corona and flame treatment work revealed that commercial loadings of antioxidants (200ppm) appear to have little effect on the treatments, the effect of a higher antioxidant level (2000ppm) was also examined.

The XPS spectra of polyethylene films pressed against poly(ethylene terephthalate) showed the expected low level of oxygen containing species. The O1s signal was higher for films containing antioxidant, and is presumably due to this material being present in the surface. Extruded samples which gave good adhesion, showed marked O1s and N1s signals. The peak areas were corrected for the different photoemission cross-sections of these core electrons to obtain atomic ratios. Values for this were obtained using pure organic films sublimed in situ in the spectrophotometer. Deconvolution of the C1s peak of treated polyethylene (spectrum 8) showed a shift of about 3eV. This is consistent with a shift of 1.5eV for -C-OH groups and 3eV for C=O groups; COOH groups give a shift of c 4.5eV. The O1s peak has a binding energy of c532eV. Most oxygen functions such as -C-OH, C=O, -C-O-C, and -O-C=O have similar binding energies (123). From the C1s and O1s peaks the most likely groups are therefore C=O and -C-OH. The sharp N1s peak has a binding energy of 399.7eV. This is consistent with $R\text{-}NH_2$. Siegbahn et al give a value of 1.6eV lower for this peak, but it was shown in section 4.3, that Siegbahn's values are consistently 1.6eV lower than those found in this work. (The difference can be explained

in differences in calibration procedures). The presence of NH_2 groups is surprising at first sight. It is suspected that nitrogen is introduced in the form of $-NO_2$ groups, by reaction with air at the high temperature used. The $-NO_2$ groups would be reduced to $-NH_2$ when aluminium foil is removed by sodium hydroxide.

XPS examination of untreated aluminium foil revealed only the expected oxide on metal and hydrocarbon C1s peak due to oil contamination during processing.

In section 4.6 it was shown that when polyethylene was melted against aluminium, O:C ratios of 3.7% and 6.9% were obtained at 150°C and 175°C respectively. The degree of oxidation of additive free polyethylene after extrusion is similar to the latter figure. This despite a very short time in the oxidation zone.

Figure 26 shows a plot of the lap shear strength against atomic O:C and N:C ratios. The two points which appear abnormally low refer to extrusion at 300°C, with and without ozone treatment, in the absence of antioxidant. Apart from these points there is an obvious correlation between degree of incorporation of polar groups (O or N containing) and the adhesion level achieved. The parallel behaviour of these parameters for any change in extrusion conditions within a series is very interesting (eg same temperature or antioxidant level, see Table 18).

The adhesion level obtained after extrusion at 280°C is reduced by the presence of antioxidant. With 0.02% antioxidant this effect is more marked at 280°C than at 300°C. This could be due to greater vaporization at the higher temperature, although the higher temperature would also help to shorten the induction time effect of the antioxidant. It is worth

noting that the same level of antioxidant did not affect the degree of oxidation for a standard flame treatment (see above). This supports the idea that with increased severity of treatment the action of the antioxidant is reduced.

A pretreatment with ozone of the polyethylene extruded at 300°C causes a substantial recovery of the adhesion levels of the samples containing antioxidant. XPS shows that "oxidation" still takes place in the same way as it does in the absence of antioxidant, ie modification of the polymer is similar especially in the O:N ratio. This suggests that ozone reacts with the antioxidant at the surface nullifying its suppressive effect on oxidation, rather than by directly oxidising the polymer via a different mechanism. This is supported by the similar levels of oxidation for the antioxidant-free specimens extruded at 300°C, with and without ozone pretreatment. Increasing the antioxidant concentration ten fold reduces the degree of oxidation considerably and decreases the adhesion to zero. Once again an ozone shower, with the attendant increase in oxidizing species imposes the oxidation and adhesion.

From the results it can be seen that heating polyethylene in air to high temperatures for a short time causes substantial oxidation and good adhesion to aluminium. Addition of antioxidants reduces the adhesion because the degree of oxidation is reduced. However, further oxidation in the case of polymer with antioxidant permits the substantial oxidation of the polymer leading to improved adhesion in spite of very high antioxidant levels. This suggests that oxidation of polyethylene is the more likely requisite for good adhesion than removal of weak boundary layers.

Willis and Zichy reported (124) similar studies in which ATR infra red spectroscopy was used to assess surface oxidation, particularly the effect of temperature and line-speed. A plot of total C=O band intensity (keto, acid and ester) normalised to the $-CH_3$ band intensity ($1375cm^{-1}$) against peel strength showed a linear correlation. They also found similar levels of oxidation for the surface against the aluminium and the outer PE surface. Both conclusions are in complete agreement with this work. The C = O bands tend to be weak, however, and no bands associated with nitrogen functions were reported. As Willis and Zichy state (124) the variability of extinction coefficients and the irreproducibility of sample-element contact in ATR make quantification very difficult. Quantification in XPS is relatively straightforward. The much greater surface sensitivity of XPS is shown by the fact that correlations between the degree of surface oxidation and adhesion for polyethylene melted against aluminium at $150^{o}C$ are also possible, using XPS, whereas ATR cannot detect oxidation under these conditions.

4.8 Use of polyethylene as the adhesive.

Bikerman (73) carried out a series of investigations into the behaviour of polyethylene used as an adhesive between metal adherends. He claimed that commercial polyethylene did not give good joint strengths. He then dissolved the polymer and reprecipitated it, and showed that low molecular weight fractions had been removed. When joints were made, using the purified polyethylene, Bikerman observed an increase in joint strength. Bikerman concluded that poor adhesion of polyethylene could be explained in terms of a weak boundary layer concept. He stated that removal of this weak boundary layer was essential if good bonding was to

ensue. As a corollary, he explained the role of pretreatments was to remove this weak boundary layer.

In the previous two sections it was found that melting polyethylene against aluminium produced a bondable surface, and that melting polyethylene for a short time at high temperatures also improved adhesion. This was thought to be contrary to Bikerman's findings and it was decided to repeat Bikerman's work. Commercial "Alkathene" WJG47, which was additive free, but otherwise not purified in any way, was melted against aluminium adherends under various conditions.

Joint strength was found to increase with temperature up to a maximum, after which it began to drop off (graph 7). However, it was noticed that polyethylene began to show signs of yellowing and embrittlement with the higher temperatures. This is due to degradation, and the lower joint strengths can be ascribed to impaired mechanical properties, which are a consequence of degradation. Previous work in this study concerned with melting against aluminium, and extrusion at high temperatures showed that oxidation in polyethylene increases with temperature. There is then little doubt that the increase in joint strength was due in large part to the increase in oxidation of the polyethylene. Increase in temperature will also cause a decrease in the viscosity of the molten polymer, and this will be better able to wet and spread on the adherend surfaces.

When the effect of "dwell time" on joint strength at constant temperature was examined, increases in adhesion occurred with increased "dwell time". With the introduction of spacers, joint strengths decreased (Table 25). Longer dwell times were needed to increase the joint strengths. The effect of spacers was to inhibit the flow of molten polymer as shown by

the presence of voids after bond rupture. This demonstrates the need for good wetting by the adhesive.

The need for oxidation to occur in this type of system has also been shown by Sykes and Hoar (125) and Bright and Malpass (83). The latter used polyethylene purified as by Bikerman (73) and found that good adhesion would only occur if oxidation was present. They showed that purified polyethylene gave no adhesion to aluminium in vacuo, but if preoxidised polyethylene was used, good adhesion in vacuo could be obtained.

The same authors in conjunction with Packham (89) have recently shown that mechanical keying is important in the case of anodised aluminium. The difference in conditions between anodised and chromic acid treated aluminium is such that mechanical keying is unlikely to play an important role in the latter case.

The XPS results of polyethylene melted against aluminium show that oxidation occurs at 150Å and 175°C. There is every reason to expect this level of oxidation to increase with higher temperatures. It can, therefore, be accepted that provided wetting is achieved, oxidation of polyethylene leads to improved joint strength.

4.9 Comparison of the adhesion levels of polyethylene and ethylene-vinyl acetate copolymers.

Sharpe (87) proposed that the main reason for poor adhesion observed with certain plastics, was due to the disparity between certain mechanical properties (such as shear modulus) of adhesive and substrate. On the basis of this, an ethylene-vinyl acetate copolymer (containing a substantial proportion of vinyl acetate) should give lower adhesion values than polyethylene when an epoxide adhesive is used. It is known

that modulus values for ethylene-vinyl acetate copolymers decrease with increasing vinyl acetate content.

It was, therefore, decided to carry out some comparative joint strength determinations for polyethylene and two ethylene-vinyl acetate copolymers to test the validity of Sharpe's contention.

The results obtained (Table 26) show that as vinyl acetate content is increased, modulus decreases. However, it can be seen that adhesion values increase with increasing vinyl acetate content. This is in contradiction to Sharpe's hypothesis.

Although XPS was not used for surface characterisation, it is possible to predict the number of polar groups in the surface. Each repeat unit of vinyl acetate will contain one carbon atom combined with oxygen. Thus the % number of oxidised carbon atoms will be half the vinyl acetate content. For the two copolymers used, this gives values of 7.5% and 12%.

Comparison of adhesion levels with oxygenated carbon content of the two copolymers and chromic acid treated polyolefin surfaces (Table 1) shows that higher adhesion levels could have been expected for the copolymers.

The reason for the relatively low adhesion levels can be explained in the following way. Most pretreatments affect only the surface and have no influence on bulk properties, except where degradation occurs. It is possible that Sharpe was partly right, increased flexibility may help to partially counteract the effect of increased polar group content.

Another explanation suggests that the nature of the oxidised group is important: In the case of ethylene vinyl acetate copolymers, the only groups available are acetate groups:-

$$\bullet CH_2 - \underset{\underset{OOC.CH_3}{|}}{CH}\bullet$$

With chromic acid treatments (section 4.3) hydroxyl, carbonyl and carboxylic groups are possible:-

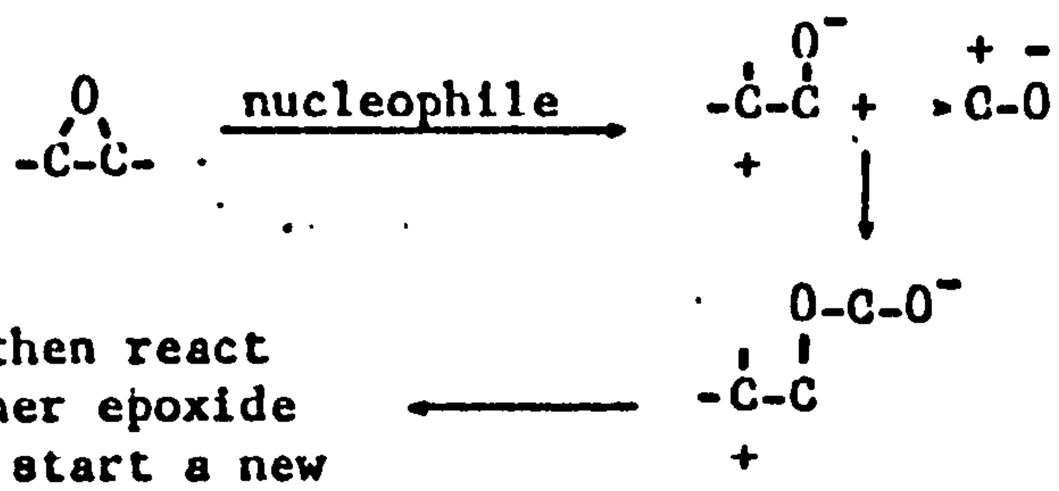
-C-OH; C=O; -O-C=O

Melting against aluminium was shown to introduce only hydroxyl and carbonyl groups:

C-OH, >C=O

The group most susceptible to nucleophilic attack is the carbonyl:-

It is the most likely of the groups to take part in reactions with epoxy adhesives possibly thus:-



4.10 Solvent extraction of Polyolefins.

If the weak boundary layer theory is correct, then polyethylene and polypropylene contain inherent weak boundary layers. These are due to low molecular weight species, present in the surface and throughout the bulk. Proponents of the theory suggest that removal of this boundary layer by solvent wiping is ineffective, since this layer is instantly replaced by migration.

The extraction experiments were undertaken with a view to remove these low molecular weight species by extraction. The idea was that if the film were extracted long enough, all the low molecular weight species would be removed and increased adhesion would result.

Increases in adhesion were obtained, but not better than 2½x for polyethylene and 4x for polypropylene. Unfortunately, environmental stress cracking of polyethylene occurred, making it impossible to pursue the experiments beyond a certain period of time.

The results of bond strength determinations on aged samples show that 28 days ageing has no deleterious effect. This could be explained in terms of very slow migration. However, proponents of the weak boundary layer concept imply migration is very rapid.

Subjecting polypropylene to trichloroethylene was a repeat of the work of Garnish and Haskins (20). These workers obtained 4-5 fold increase in joint strength. This is similar to the data in Table 22. Polyethylene disintegrated in the vapour, and was therefore dipped into solvent at 20°C. No increases in adhesion were found.

Garnish and Haskins presented evidence to show that the surface of their treated polypropylene was considerably roughened. Talysurf work shows that there is some roughening of the extracted polyethylene surface. Since roughening will increase the surface area, this is the most likely explanation of the improvements in adhesion.

4.11 Ammonium persulphate and peroxide treatments.

Morris (10) carried out her work using a high density polyethylene and obtained substantial increases in adhesion. No increase in surface oxidation was found by means of ATR spectrophotometry, although an increase in wettability was observed. Since a cross-linked layer was found, Morris concluded that the increase in adhesion was due to weak boundary material being cross-linked to the surface. Similar work with a low density polyethylene, in this study provided similar results. The amount of cross-linked material was considerably lower. Contact

angles show a large,decrease. In view of the previous agreement between XPS and contact angle determinations it is reasonable to assume that substantial oxidation of the surface has occurred, although not to a depth sufficient for ATR determinations.

Brewis carried out studies on high density polyethylene dipped in peroxide solutions (35). He found that temperatures of 120°C were necessary before an increase in adhesion occurred.

The object here was to repeat the work of Brewis and see if high adhesion could be obtained, using a low density polyethylene. The results obtained showed that at best a 2 fold increase in adhesion was obtained. Bragole (11) subjected polyethylene to dipped in peroxide solutions to UV light and obtained good adhesion. The relative lack of success with this treatment is probably due to the low temperatures employed. It would appear that at temperatures below 120°C the activation energy of polyethylene is too high for appreciable oxidation to occur. Presumably the UV radiation used by Bragole was sufficient for this purpose. Higher temperatures could not be used in the case of low density polyethylene, because it melted at about 95°C.

4.12 Pretreatments of Polytetrafluoroethylene

The results of treating PTFE by electrochemical attack are shown in Tables 27-29. In all cases there is an increase in the adhesion level of the polymer. In the case of direct contact, there is blackening observed at the point of contact. The extent of blackening is partly dependant on the voltage applied. The nature of blackening was found to be non-uniform. The blackening grew outwards much further in the direction of skiving marks than at right angles to it. This suggests some degree of anisotropy in the PTFE surface during the process of

skiving. Confirmation of this has come from Barker et al (126). These workers examined a number of PTFE samples with different processing histories. The materials included pressed sheet, skived tape, unsintered calendered film and ram extruded rod. It was found that electrochemical etching was highly anisotropic for ram extruded rod and unsintered calendered rod; skived film showed some anisotropy, while there was no preferential rate of attack for pressed sheet. Removal of about 3μm of surface from ram extruded rod caused electrochemical attack to become isotropic. This concluded Barker et al showed that manufacturing processes could cause a high degree of orientation in the surface of PTFE. Since electrochemical attack is believed to proceed via conducting carbon, the alignment of chains during orientation would give rise to the effect observed.

When naphthalene and other compounds capable of forming radical anions were used, the surface was found to progressively darken till a black shiny surface was obtained. SEM Studies revealed no changes in surface topography. Ageing of the treated surfaces showed that initially the black surface lost its sheen and with time the black surface became lighter in colour. Eventually a light grey surface was obtained. SEM shows that a small amount of carbonaceous film remains on the surface.

Treatment with concentrated nitric acid caused the black layer to be removed and a yellow surface with unimpaired adhesion was obtained. Treatment with fuming nitric acid gave a white to off-white surface with much reduced adhesion levels. XPS studies were limited to films treated when a lead electrode was used. These showed that de-fluorination of

surface occurred and that a carbon layer with oxygen containing species was being formed. Further treatment was obscured by a layer of lead. However, treatment with concentrated nitric acid removed this and showed that a large proportion of the fluorine signal was restored. Oxygen containing species were still present. Dwight and Riggs (90) who treated FEP with sodium in ammonia and examined the surface with XPS showed a similar defluorination of surface after treatment, with an increase in oxygen containing species. Reacting the treated surface with sodium hypochlorite solution restored the original colour to the film and adhesion levels were not altered significantly. Their XPS spectrum revealed the re-emergence of the fluorine peak but there was still a considerable oxygen peak. In view of the work carried out with polyethylene, the oxygenated species formed are probably responsible for the increased adhesion. Treatment with fuming nitric acid caused a considerable decrease in adhesion values. It is probable that this very severe treatment causes oxidation of the remaining carbon and oxidised species in the surface to carbon dioxide and other small molecules which are then removed from the surface. Further work with XPS will be necessary to confirm this, but it is the most probable answer.

The mechanism of these treatments has not been definitely established. It is probable that simple electron transfer is involved, either from the naphthalene radical anion or directly from the solvent. This mechanism is consistent with the fact that strongly electropositive metals (127) or their amalgams (128) react directly with polytetrafluoroethylene to give the blackened surface characteristic of all the above reactions.

Jansta and Dousek (128) found that carbon formed on reduction by lithium amalgam to be conducting and thus capable of conveying electrons from

the amalgam to unreacted polytetrafluoroethylene. The fact that during electrochemical reduction the area of attack extends some way from the point of contact strongly supports the above mechanism. For one of the treated films the thickness of treated surface area was estimated on the basis of weight loss measurements to be about 150nm thick. Surface conductivity measurements of treated film were made, but little change was found. Since these determinations were carried out on film in air, this would be due to rapid oxidation of the film on exposure to air. Barker et al (129) who examined the carbonaceous layer formed after electrochemical pretreatment found that if oxidation of the newly formed carbonaceous could be prevented, then the film was conducting. Exposure to air led to an appreciable increase in the resistance of the film.

Treating bronze filled polytetrafluoroethylene does not increase adhesion levels substantially. The adhesion values obtained for untreated film are relatively high. This is due to bronze particles, which constitute 27% of the film, acting as good sites for bonding. Improving the adhesion of the polytetrafluoroethylene will thus have very little effect.

While the two methods of pretreatment discussed have as yet little commercial significance, they do have certain possible applications. They show that the need for dangerous alkali metal solutions and amalgams is not essential. The direct contact method could be applied to treatment of films and articles on one side only. It has the added advantage of being able to be carried out in air. A suitably devised form of brush electrode is needed. With radical anions the main disadvantage is the need for long treatment times and high current, are uneconomical compared with present treatments. However, with suitable improvements in cell design, choice of semipermeable membrane, solvent and support

electrolyte it should be possible to generate radical anions in sufficiently high concentration to reduce treatment times.

4.13 General Discussion of the Pretreatments.

Examination of the effect of the various pretreatments, on polyolefins and polytetrafluoroethylene, reveals the inadequacy of ATR infra red spectroscopy as a technique for studying surface chemical changes. This technique is insensitive since it requires a relatively large depth of treatment, which most commercial treatments do not achieve. As can be seen from the foregoing discussion, it has been responsible for many erroneous conclusions to be formed. The usefulness of XPS as a surface study technique has been amply demonstrated. Although, it could only be made use of sparingly, it has provided a wealth of data. It has shown that contact angles can be a very good guide to changes in surface chemistry, provided due allowance is made for the effect of surface roughness upon it.

The results of the pretreatments indicate that increases in adhesion levels are accompanied by oxidation of the surface. This is found both for polyolefins and for polytetrafluoroethylene. In the case of pretreated polytetrafluoroethylene, when the oxidised layer is removed, the adhesion levels drop dramatically.

Many of the treatments show a positive correlation between the level of oxidation as determined by XPS and joint strengths. There is no doubt that in certain cases the oxidation values are very high and can be partly explained in terms of overtreatment. It is in this context useful to consider the degree of oxidation needed to give good adhesion. The best example is polypropylene. The slight difference between oxidation levels after normal and overnight washing of film treated for 6 hours at

70°C in chromic acid, suggests that few low molecular weight oxidised species are left on the surface. The lap shear strength is approximately 40x greater than that of untreated film, and similar to values obtained with poly(ethylene terephthalate) using the same adhesive (35). Assuming that carbon is associated with oxygen in a 1:1 ratio (ie C-OH or C=O), about 5% of the carbon atoms in treated polypropylene will have oxygen containing groups associated with them. For comparison the O:C ratio in poly (ethylene terephthalate) is 0.2 (if C-O-C linkages are ignored) ie about 3x greater than that of the polypropylene sample. (This assumes that the chains of poly(ethylene terephthalate) are lying parallel to the surface). This suggests that sufficient interaction between substrate and adhesive can be achieved with a low degree of oxidation.

With the knowledge that low molecular weight oxidised species are present on the surface, future work should endeavour to remove these, by means of suitable solvents to ensure that only oxidised groups present in the true surface are left. More meaningful data as to oxidation levels required for good bonding will be obtained. This does not mean that present results have little value. The opposite is true, since they show that extensive oxidation has occurred, where previously none was thought possible.

Other workers have begun to use XPS and their results reinforce the present findings that oxidation is related to improved adhesion. Thus Dwight and Riggs (90) have shown that melting FEP against gold shows that oxidation of the surface occurs, contrary to the findings of Hara and Schonhorn (78). Blyth and co-workers examined the effect of discharge in noble gases on polyethylene. Their method was very similar to Schonhorn's CASING. Once again, oxidation of the surface was found. Schonhorn claimed to find no oxidation and explained increased adhesion

as due to cross-linked layer being formed. There can be no doubt that cross-linking does occur in such a system. There is also evidence of some cross-linking of polyethylene with chromic acid treatment. If cross-linking were the sole answer, then γ irradiation of samples under nitrogen should produce comparable increases in bond strength. The work of Brewis (35) shows that adhesion does not improve. It is possible that conditions were not suitable, but when irradiation occurred in air, there was a significant increase in adhesion levels. This is not surprising in view of the previous discussion, since cross-linking by itself can only improve the mechanical properties, while incorporation of oxidised species leads to increased adhesion.

4.14 Discussion of the Results in view of current theories.

It is generally accepted that the Diffusion and Electrostatic theories do not explain the need for pretreatments to polyolefins and polytetrafluoroethylene. The mechanical theory has on the whole been discounted. The arguments used being that even extensive roughening of the surface does not lead to large increases in bond strength (130). Recently Packham et al have shown that adhesion of polyethylene to unsealed anodised aluminium can only be explained in terms of mechanical keying (89). It is interesting to speculate whether this is a special case, or whether in spite of their precautions, some oxidation did occur. Certainly small increases in adhesion such as in extracted polyethylene could be explained purely in terms of changed topography. However, in the case of anion naphthalene radical-treated polytetrafluoroethylene, no change was found in surface topography, and this is borne out by others (129). The increase in adhesion is considerable. This theory then cannot explain the large increases in adhesion obtained.

This by a process of elimination leaves only the Adsorption and Weak Boundary Layer theories to consider. Of the two theories, the weak boundary layer concept has enjoyed the most support. In general, it is a very good theory and there is much practical evidence in its favour. Its recommendations that surfaces must be clean before good bonding will occur, are widely obeyed in industry. Many instances of "poor" joints on examination reveal contamination in the form of weak boundary layers such as grease, dirt, etc. However, in respect of polyolefins and polytetrafluoroethylene, this theory relies on assumption that these polymers contain an inherent weak boundary layer. This boundary layer contains processing aids and low molecular weight material. The main disadvantage of this assumption is that no one has actually isolated such a weak boundary layer. Bikerman dissolved polyethylene in solvents and reprecipitated it, eliminating low molecular weight material. With the purified polethylene he obtained increased adhesion to metal (73). However, his conditions were such that similar work carried out in this project with unpurified polyethylene, gave equally good results. Bright and Malpass (84) using purified polyethylene could not obtain good bonds in vacuo. It is true that Schonhorn has claimed that melting polyethylene in contact with its own vapour leads to formation of a weak boundary layer (131), but in the case of purified polyethylene, where would this weak boundary layer material come from. Bright and Malpass then preoxidised some polyethylene which when melted under identical vacuum conditions, gave high bond strengths. The weak boundary layer material should have reappeared in this case as well, but it did not. Perhaps there is no inherent weak boundary layer. It can be argued that the weak boundary layer in treated polyethylene is displaced by the adhesive. However, in this case, it would be reasonable to assume

that it should be displaced in untreated polyethylene as well.

During the experimental work, the question of whether inherent weak boundary layers are important in determining adhesive strengths of polyolefins was investigated by a study of epoxy resin surfaces cured (a) in air, and (b) in contact with untreated polyethylene which was subsequently removed in a lap shear test. XPS did not reveal any residual polyethylene on the epoxide surfaces; the carbon spectra of both surfaces were identical. However, the O1s:N1s peak ratios differed sufficiently to indicate a somewhat different surface composition for the two surfaces. This is hardly surprising, since hardener and other volatiles were more likely to escape from the surface cured in air. This is evidence against the weak layer concept. Proponents of this theory have argued that transfer of weak layer material does occur. Further evidence against this concept comes from extraction experiments. Schonhorn and Hansen claim that since hexane-heptane mixtures do not swell the polymer to an appreciable extent, the weak boundary layer material is removed, giving rise to increased bond strengths. This increase in bond strength is relatively low, about 2x. It could be argued that perhaps not enough material was removed. However, much longer times did not increase adhesion levels. The low molecular weight material in the bulk should migrate to the surface, but ageing of up to one month revealed no decrease in bond strength.

Nucleation against aluminium was said to produce a transcrystalline region capable of good bonding. Nucleation against poly (ethylene terephthalate) has also been found to give a transcrystalline region but not an increase in bond strength.

"CASING" was stated to produce a cross-linked surface, which was free

from oxidation, and which gave good adhesion. Others have shown that oxidation does occur (86, 91).

A further argument against the weak boundary layer concept is the fact that aluminium foil, even after degreasing and chromic acid etching, still has a hydrocarbon layer attached to its surface. This could act as a true weak boundary, but it has been shown that the aluminium can form strong bonds with polyethylene.

From the above considerations, there is a considerable body of evidence against the concept that polyolefins and polytetrafluoroethylene have an inherent weak boundary layer. In every case that has been previously cited as evidence for the weak boundary layer, there is an alternative explanation. This is that oxidation is introduced by the pretreatments. If the results obtained are examined in terms of Adsorption Theory then a different picture is obtained. There is better agreement between the theory and the results. The theory requires that polar groups be introduced into the surface. The available XPS results bear this out. Corona discharge and flame treatments introduce polar groups into the surface. Melting in contact with aluminium shows an increase in adhesion and oxidation levels. Melting against poly (ethylene terephthalate) does not increase oxidation, but then adhesion is poor. Extrusion at high temperatures shows evidence of increases in both oxidation and adhesion levels. Addition of antioxidant lowers both values, but treatment with ozone causes recovery in both. Even with extremely mild chromic acid treatments, there is evidence of considerable oxidation, even in the case of polypropylene, previously believed by some not to oxidise by even very severe treatment. The polytetrafluoroethylene pretreatments are also shown to

cause increased adhesion with increased oxidation.

For the treatments where XPS measurements were not undertaken there is other evidence of oxidation. In the case of the persulphate treatment there is a considerable decrease in contact angle. (XPS studies show that contact angles can be a good guide to surface chemical changes). The experiments in which polyethylene was used as the adhesive were not followed by XPS or contact angle studies. But the evidence from melting polyethylene against aluminium and extrusion onto aluminium, shows that more oxidation occurs with higher temperatures.

5. Conclusions.

The aim of this project was to increase the understanding of the factors involved in the adhesion of low energy substrates. One of the main objectives was to examine the importance of weak boundary layers. A minor objective was to examine Sharpe's contention that it was the large difference in modulus values between adhesive and substrate which was responsible for poor bonding.

In the case of the latter, evidence was presented which showed that increasing modulus differences did not cause adhesion levels to decrease. Ethylene-vinyl acetate copolymers gave higher joint strengths with epoxy adhesives than polyethylene, even though the modulus difference increased. Sharpe's contention that modulus differences were the main reason for poor adhesion was thus disproved. However, it could be still used as a partial explanation in certain cases.

Research into the effect of pretreatments of this study revealed the following:-

1. That contrary to previous findings, very mild chromic acid treatments introduced polar groups into the surface of polyolefins. The increase in concentration of oxidised groups is related to increased adhesion.
2. Melting polyethylene against aluminium gives rise to substantial surface oxidation and increased adhesion in contradiction to the work of Hansen and Schonhorn.
3. Polyethylene can be used as an adhesive without the need for previous purification. The increase in joint strengths with increase in temperature can be explained in terms of high oxidation and better wetting of substrate by molten polyethylene.
4. Flame and corona discharge treatments are shown to induce oxidised

groups into poly-olefin surfaces. The increase in content of oxygenated species is matched by increased adhesion.

5. Extrusion of polyethylene at high temperatures gives rise to oxidised and bondable surfaces. Incorporation of antioxidant causes the oxidation and adhesion levels to drop. Further oxidation by means of ozone treatment restores both adhesion and oxidation levels. This is explained best in terms of oxidation causing increased adhesion rather than in terms of weak boundary layers.
6. There is little decrease in bond strength if treated samples are stored with care. No weak boundary material migrates to the surface to cause a decrease in adhesion.
7. Attempts to remove weak boundary material by solvent extraction result in small to moderate increases in adhesion. The improvements in adhesion can be best explained in terms of greater surface area and mechanical keying.
8. Electrochemical pretreatments of polytetrafluoroethylene give rise to an oxidised surface layer, which results in improved adhesion. When this layer is removed, a considerable decrease in adhesion results.
9. There is no evidence of weak boundary layer transfer to epoxy adhesive from untreated polyethylene, although the small molecules may have been evaporated by the high vacuum used.

None of these items of evidence on its own provides conclusive evidence against the weak boundary layer concept. However, taken together, they provide strong evidence to show that weak boundary concept does not explain the adhesion characteristics of polyethylene, polypropylene and polytetrafluoroethylene.

The research described in this thesis has demonstrated the usefulness of X-ray photoelectron spectroscopy as a technique for examining the adhesion problems involving polymer surfaces. The technique has provided much useful information on the surface treatments examined. In particular, it has identified the groups introduced; it has given a measure of their concentration; and it has been possible to estimate the depth of treatment in some cases.

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